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Contents of Volume

Number 1

Directly Bonded ^{13}C–^{13}C Spin–Spin Coupling Constants in Structural Studies 1
L B Krivdin, G A Kalabin

Metal Carbonyl Catalysts of the Synthesis of Organic Compounds from Carbon Monoxide and Molecular Hydrogen 17
A L Lapidus, M M Savel'ev

Reactions of Free Radicals with Organic Cations 29
V I Bogillo, I P Gragerov

Nucleophilic Substitution in Hexachlorocyclopentadiene 41
S A Ismailov

Reactions Involving the Addition of Dithio-acids to Unsaturated Compounds 52
V N Drozd, M L Petrov, N Ya Kuz'mina, A S Vyazgin

Rearrangements with Migration of a Fluorine Atom 62
L S Kobrina, V N Kovtonyuk

Steric Structuring of Polyolefins by Chemical Methods 72
I V Konoval, N G Konovalenko, S S Ivanchev

Electrophoretic-electrochemical Deposition of Polymers and Metals 82
Yu F Deinega, Z R Ul'berg

Number 2

Trends in the Development and Tasks of Modern Quantum Chemistry 97
N D Sokolov

Layered Silicates as Catalysts 115
M I Rozengart, G M V'yunova, G V Isagulyants

Metal Complex Catalysis of Electrode Processes 129
O N Efimov, V V Strelets

The Oxidation-reduction Stage in the Nitration Reaction 144
A S Morkovnik

Selenonium Compounds and Their Applications in Synthesis 161
N N Magdesieva

The Structure of Polymeric Colloid Particles and the Effect Associated with It 174
V I Eliseeva

Number 3

Topological Indices in Organic Chemistry 191
M I Stankevich, I V Stankevich, N S Zefirov

Lanthanide Oxide Sulphides 209
Yu L Suponitskii, G M Kuz'micheva, A A Eliseev

Oxidative Condensation of Methane — a New Pathway to the Synthesis of Ethane, Ethylene, and Other Hydrocarbons 221
Kh M Minachev, N Ya Usachev, V N Udut, Yu S Khodakov

The Reactions of Compounds with Halogenoimidoyl Groups 234
T D Petrova, V E Platonov

General Principles and Characteristics of Cyclopalladation Reactions 250
V V Dunina, O A Zalevskaya, V M Potapov

Photochemical Methods for the Construction of an Additional Four-membered Carbocycle in Steroids 270
A V Kamernitskii, V N Ignatov, I S Levina

Mechanochemical Synthesis 283
C Simionescu, C V Oprea

Number 4

Substitutional Carbonylation of Organic Compounds Catalysed by Palladium Complexes 299
Yu V Gulevich, N A Bumagin, I P Beletskaya

The Kinetic Stability of Biscyclopentadienyl and Diarene Compounds of Transition Metals in the Thermal Decomposition Reaction 316
L M Dyagileva, E I Tsyganova, Yu A Aleksandrov

Oxidative Chlorination of Aliphatic Hydrocarbons and Their Chloro-derivatives 326
Yu A Treger, V N Rozanov, M R Flid, L M Kartashov

Stable Methylenequinones 336
A A Volod'kin, V V Ershov

Carcinogenic *N*-Nitrosamines. Formation, Properties, and Analysis 350
Ya L Kostyukovskii, D B Melamed

The Preparation, Structure, and Properties of Semiconductor Films Based on Acetylenic Polymers 367
A A Matnishyan

Modern Methods of Synthesis of Modified Glycerophospholipids 382
O V Bogomolov, A P Kaplun, V I Shvets

Number 5

Application of Quantum-chemical Methods to the Diels–Alder Reaction 397
S S Babichev, V A Kovtunenko, Z V Voitenko, A K Tyltin

Metal-carboxylic Acids and Their Derivatives 406
I S Kolomnikov, T V Lysyak, S L Rusakov, Yu Ya Kharitonov

Coordination Compounds of Transition Metals in the Chemistry of Aromatic Nitro-compounds 419
E N Izakovich, M L Khidekel'

The Structure and Electron-donor Properties of Organic Compounds of Selenium(II) 433
E N Gur'yanova

Organosilathianes 447
M D Mizhiritskii, V O Reikhsfel'd

The Structure and Properties of Highly Conducting Polyacetylene Complexes 461
V M Skorobogatov, I V Krivoshei

The Glass Points and Dielectric Relaxation of Carboxyl-containing Copolymers and Ionomers Based on Them 475
I A Ionova, Yu B Monakov, S R Rafikov

Number 6

Problems in the Physical Chemistry of Membrane Processes 485
Ya M Kolotyrkin

From Biological to Synthetic Membranes 487
S F Timashev

Modern Ideas About Diffusion in Polymer Systems 504
A E Chalykh, V B Zlobin

Molecular-kinetic Models of the Transfer of Substances in Inorganic Membranes 520
Yu K Tovbin

A Phenomenological Theory of Diffusion in Heterogeneous Media and Its Use in Describing Membrane Separation Processes 530
I N Bekman, I P Romanovskii

Methods for Obtaining Polymeric Membranes 539
L P Perepechkin

Selectively Permeable Polymers and Gas-separation Membranes: Structure and Transport Properties 549
S G Durgar'yan, Yu P Yampol'skii, N A Plate

The Role of Interphase Phenomena in the Processes of Ion Transport Through Liquid Membranes 559
V V Tarasov, A A Pichugin

New Trends in the Development of Polymeric Materials for Reverse Osmosis Membranes 566
Yu E Kirsh, Yu M Popkov

Modelling Reverse Osmosis 572
S S Dukhin, N V Churaev, V N Shilov, V M Starov

Concentration Polarisation in the Electrodialysis Process and the Polarisation Characteristics of Ion-selective Membranes 585
E M Balavadze, O V Bobreshova, P I Kulintsov

Bacteriorhodopsin as a Possible Element of Membrane Bioreactors 592
A V Maksimychev, S K Chamorovskii

Number 7

Relaxation and Two-dimensional Phase Transitions in the Electrical Double Layer 605
V A Benderskii, G I Velichko

Photonics of the Triplet States of Molecular Complexes 620
E I Kapinus, I I Dilung

The Study of the Boundary Viscosity of Organic Liquids by the Blow-off Method 634
B V Deryagin, V V Karasev

Reactions of Saturated Cyclic Sulphides 648
E N Karaulova

Transition Metal Percarboxylates, Alkylperoxides, and Hydroperoxides 668
V M Fomin, V N Glushakova, Yu A Aleksandrov

Polymeric Chemical Fibre-reinforced Composite Materials with Reduced Combustibility 680
L G Panova, S E Artemenko, N A Khalturinskii, A A Berlin

Chemical Principles of the Biotechnology of the Preparation of Fuel 687
S D Varfolomeev, S V Kalyuzhnyi, D Ya Medman

Number 8

The Influence of Surface Microstructures on the Physicochemical Properties of Oxides 705
A I Leonov, Yu P Kostikov, V S Strykanov

The Paramagnetic Hydrophilic Probing of Colloidal Systems by NMR Spectroscopy 717
Yu E Shapiro

Spectroscopy of Molecules and Molecular Complexes Dissolved in Liquefied Gases: Structure and Reactivity 730
Ya M Kimel'fel'd

Photoelectron Spectroscopy of Organofluorine Compounds 745
M E Akopyan, A V Golovin, A A Rodin, Yu L Sergeev

Oxidative Substitution of Halogen Atoms in Organic Halogeno-derivatives — a New Type of Nucleophilic Substitution Reactions at a Saturated Carbon Atom 760
L S Boguslavskaya, N N Chuvatkin, A V Kartashov

The Synthesis and Complex Forming Capacity of Phosphorus-containing Macrocycles 776
E N Tsvetkov, A N Bovin, V Kh Syundyukova

Dissociation of Water Molecules in Systems with Ion-exchange Membranes 801
V I Zabolotskii, N V Shel'deshov, N P Gnusin

Number 9

Martin Izrailevich Kabachnik 809
P M Valetskii

Interaction of Refractory Metal Oxides with Carbon 810
A G Vodop'yanov, G N Kozhevnikov, S V Baranov

Photon Transfer Reactions in Free Radicals. Spin pH Probes 824
V V Khramtsov, L M Vainer

NMR Spectroscopy of Polyfluorinated Allyl Cations 839
V I Bakhmutov, M V Galakhov

Fluoroalkenylphosphonates 852
A A Kadyrov, E M Rokhlin

The Use of Electrochemical Methods for Studying the Structure and Reactivity of Organometallic Compounds 864
T V Magdesieva, K P Butin, O A Reutov

Polymers Based on Unsaturated Derivatives of Carbaboranes 875
O A Mel'nik, A A Sakharova, T M Frunze

Phosphite Synthesis of Oligodeoxyribonucleotides 886
N N Karpyshev

Future Outlook for the Construction of Biologically Active Compounds 897
O A Raevskii, A M Sapegin

Number 10

Vasilii Vladimirovich Korshak 911
P M Valetskii

Short-range Order and Local Displacements of the Atoms in Non-stoichiometric Compounds 913
A I Gusev

The Anisotropy of Molecular Magnetic Susceptibility and Its Structural-chemical Aspects 929
S G Vul'fson

NMR Spectroscopy of Azo Dyes 941
L A Fedorov

Analytical Gas Chromatography of Volatile Metal Complexes 956
D N Sokolov

The η^5-Indenyl and η^5-Fluorenyl Complexes of Transition Metals and Their Comparison with the η^5-Cyclopentadienyl Compounds 967
I A Lobanova, V I Zdanovich

Microlayer and Glass Formation in Block Copolymers 981
Yu D Shibanov, Yu K Godovskii

Specific Pyrolysis of Polycondensation Polymers 999
L G Gladkova, E F Kolpikova, Ya S Vygodskii, A S Fialkov

Number 11

The Influence of the Surface on Phase Transitions in Two-component Systems 1013
A I Dolinnyi, V A Ogarev

Oxidation of Sulphur Dioxide in Aqueous Solutions 1029
V A Golodov, L V Kashnikova

The Synthesis and Properties of Covalent Organic Perchlorates 1041
N S Zefirov, V V Zhdankin, A S Koz'min

Aryl Derivatives of Thallium(III): Preparation and Use in Organic Synthesis 1054
A Ya Usyatinskii, V I Bregadze

The Anomalies of the Increase in Viscosity in Binary Polymer Systems 1069
S M Mezhikovskii, E I Vasil'chenko, Sh A Shaginyan

Kinetics and Mechanism of the Inhibited Polymerisation of Vinyl Monomers 1083
M D Gol'dfein, G P Gladyshev

Methods for the Separation and Quantitative Determination of Nucleotides, Nucleosides, and Bases 1098
S N Zagrebel'nyi, V I Pupkova, Yu L Khripin

Number 12

Modern Ideas About the Mechanisms of Homogeneous and Heterogeneous Acid Catalysis: Similarities and Differences 1109
V B Kazanskii

The Phase Boundary Potentials at the Interface between Two Immiscible Electrolyte Solutions 1124
V S Markin, A G Volkov

Contemporary Ideas About the Conformations of Eight-membered Cyclic Systems with Planar Fragments 1142
R P Arshinova

Reactions of Transition Metal Polyhydride Complexes with Hydrocarbons 1162
V D Makhaev, A P Borisov

Agostic Hydrogen Atoms in Transition Metal Complexes 1175
A G Ginzburg

Dibenzylideneacetone Complexes of Transition Metals 1194
A Z Rubezhov

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Directly Bonded $^{13}C-^{13}C$ Spin-Spin Coupling Constants in Structural Studies

L.B.Krivdin and G.A.Kalabin

The review presents the present state of research into the directly bonded $^{13}C-^{13}C$ spin-spin coupling constants (SSCC)—the parameters of NMR spectra which are most difficult to measure and which contain unique structural information. The principal factors determining the magnitude of the direct $^{13}C-^{13}C$ SSCC, namely the hybridisation of the interacting atoms, the electronic influence of substituents, steric and solvation effects, and the influence of the unshared electron pairs of the heteroatoms, are analysed. The possibilities of using the directly bonded $^{13}C-^{13}C$ SSCC for the solution of a wide variety of structural problems in chemistry are examined; special attention is devoted to the prospects for the employment of these parameters in stereochemistry and conformational analysis.
The bibliography includes 232 references.

CONTENTS

I. Introduction	1
II. The nature of the spin-spin coupling between directly bonded carbon nuclei	3
III. The principal factors determining the variation of the directly bonded $^{13}C-^{13}C$ SSCC	4
IV. Structural applications	9

I. INTRODUCTION

The measurements of the constants for the spin–spin coupling between ^{13}C nuclei ($^{13}C-^{13}C$ SSCC or $^{n}J_{SS}$) under the conditions of the natural abundance of this isotope (~1.1%) involves the recording of the ^{13}C NMR spectra of molecules containing simultaneously two ^{13}C nuclei. The fraction of such molecules in the natural mixture of isotopomers is only ~0.01%, i.e. one molecule out of 10 000. This fact and also the low relative sensitivity of the ^{13}C NMR method make the $^{13}C-^{13}C$ SSCC the parameters of the high-resolution NMR spectra of organic compounds which are most difficult to obtain.

The first studies involving the experimental measurement of $^{13}C-^{13}C$ SSCC date back to the beginning of the 1960s [1-3] and were carried out for model compounds enriched in ^{13}C. The complexity of the synthesis of a wide range of such compounds was one of the reasons why such studies have been non-systematic during the last 10–15 years. The situation changed significantly at the end of the 1970s with the appearance of commercial Fourier Transform NMR spectrometers improved by the incorporation of pulse type programmers and highly sensitive devices for the recording of the signal ensuring a real increase of the sensitivity of the method, amounting on average to two orders of magnitude. Together with successes in the synthesis of ^{13}C-labelled compounds, this led to a vigorous growth of studies on the $^{13}C-^{13}C$ SSCC.[4-10] Thus, whereas in 1979 about 700 experimental values of the direct $^{13}C-^{13}C$ SSCC ($^{1}J_{CC}$) were known, in 1981 as many as approximately 1800 were measured.[10]

The method for the observation of ^{13}C satellites in the ^{13}C NMR spectra under the conditions of the "suppression" of the signals of the principal isotopomers, developed by Bax,

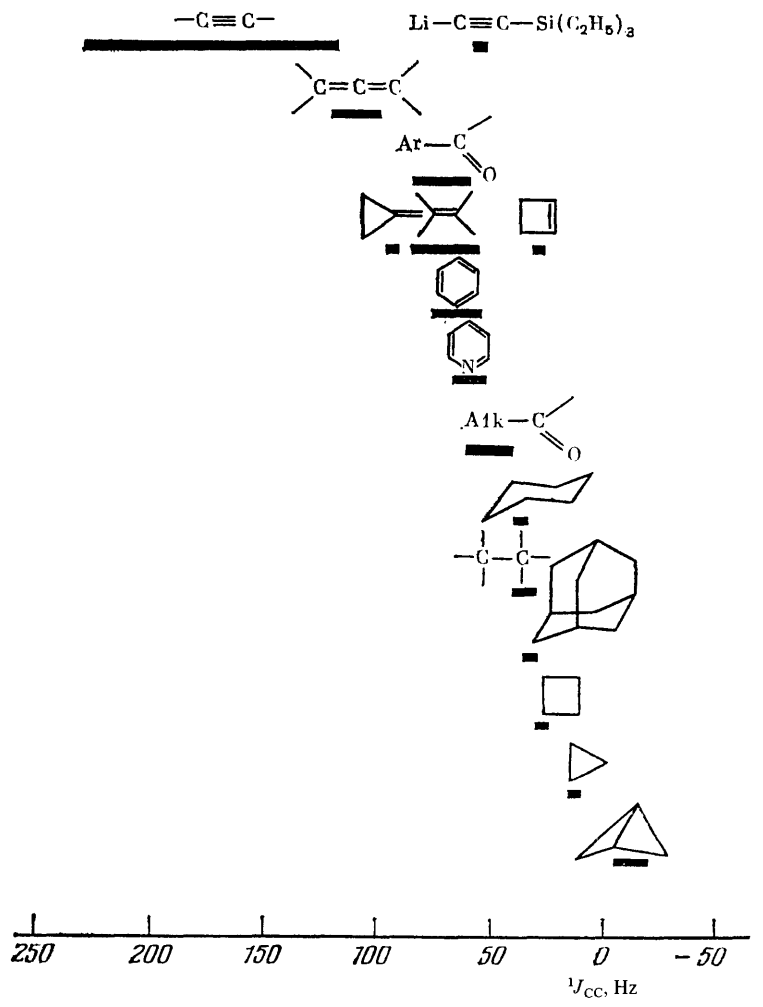


Figure 1. The ranges of variation of the directly bonded $^{13}C-^{13}C$ SSCC for different classes of organic compounds.[8,9]

Freeman, and Kempsell,[11,12] occupies a special place in the development of the research into the $^{13}C-^{13}C$ SSCC. The essential feature of the method, which the authors called INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment), consists in the conversion of the magnetisation of the satellites into the "two-quantum coherence" state $\mathcal{F}_2$ with subsequent separation of the components of $\mathcal{F}_2$ and the component of magnetisation $\mathcal{F}_0$ corresponding to ^{13}C nuclei without $^{13}C-^{13}C$ SSCC. Without increasing the sensitivity compared with the usual procedure for the recording of ^{13}C signals, the method facilitates significantly the measurement of weak signals due to $^{13}C-^{13}C$ SSCC in specimens with a natural isotopic content, because it eliminates the problem of their overlap with the strong signals of the main isotopomers, the signals of impurities, and also the signals modulated by the rotation of the tube. A two-dimensional version of the basic inadequate INADEQUATE method [13–15] and also a version which has been modified and combined with certain other pulse sequences[16–24] were realised subsequently. As a result, the measurement of $^{13}C-^{13}C$ SSCC on modern spectrometers has now become just as easy as the recording of the ^{13}C NMR spectra themselves 15 years ago.

This review surveys the available data solely on the directly bonded $^{13}C-^{13}C$ SSCC, because the geminal, vicinal, and long-range $^{13}C-^{13}C$ constants have already been the subject of a recent careful examination.[8,9] As can be seen from the correlation diagram presented (Fig.1), the range of variation of the directly bonded $^{13}C-^{13}C$ SSCC is exceptionally large: from −20 Hz in bicyclobutanes to +230 Hz in acetylenes.† Their information content is also high, because the accuracy of the measurement of these SSCC is to within 0.1 Hz and less. Attention is concentrated on the principal applications of $^1J_{CC}$ which have arisen in the solution of a wide variety of structural problems of organic chemistry such as the use of $^1J_{CC}$ in stereochemistry and conformational analysis, the study of the effects of substitution and the

† The few experimental measurements of the signs of $^nJ_{CC}$ suggest that all the direct and vicinal $^{13}C-^{13}C$ SSCC are positive (with the exception of sterically strained systems of the bicyclobutane series), while the geminal constants are of variable sign.[5,6]

properties of substituents, the establishment of methods for the biosynthesis and the determination of the structures of complex synthetic and natural products, and the structural studies of the nature of the carbon–carbon bond (estimation of the amounts of *s* character, i.e. of the contributions of the 2*s* orbitals of the carbon atoms to the corresponding hybrid atomic orbitals, of the degree of hybridisation of the interacting atoms, of the bond lengths and bond force constants, and certain other important characteristics). The experimental results of individual studies are resorted to to a minimal extent and are used as specific examples. The consideration of the structural applications of the directly bonded $^{13}C-^{13}C$ SSCC is preceded by sections dealing with the state of the theoretical calculations of these constants and the analysis of the structural factors determining their values.

II. THE NATURE OF THE SPIN–SPIN COUPLING BETWEEN DIRECTLY BONDED CARBON NUCLEI

Calculation of the directly bonded $^{13}C-^{13}C$ SSCC on the basis of the modern theory of spin–spin coupling do not as a rule lead to quantitative agreement with experiment, but make it possible in a number of instances to understand the principal trend in the variation of the experimental values of $^1J_{CC}$. This Section deals briefly with the main results of the theoretical study of $^1J_{CC}$; a more detailed discussion of the theoretical problems and of the problem concerning the calculation of $^1J_{CC}$ may be found elsewhere.[25,26]

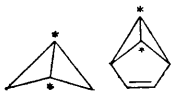
1. The Coupling Mechanisms

The magnetic moments of two directly bonded ^{13}C nuclei interact via the spin polarisation mechanism. The directly bonded $^{13}C-^{13}C$ SSCC corresponding to this interaction are determined by three contributions arising via three independent mechanisms of the spin–spin coupling: the Fermi-contact mechanism (contact electron–nucleus interaction), the spin–orbital mechanism (the interaction of the orbital electron currents with the nuclear moments), and the dipole–dipole mechanism (the interaction of electronic and nuclear dipoles).[27]

The Fermi-contact contribution is proportional to the product of the *s* orbital densities at the corresponding nuclei, while the two non-contact contributions are proportional to the products of the one-centre integrals of the valence *p* electrons of the interacting carbon nuclei. The first acceptable algorithm for the calculation of the above contributions was proposed by Blizzard and Santry,[28,29] who established that in many instances the Fermi-contact contribution only is sufficient for the calculation of $^1J_{CC}$; the inclusion in the calculation of the non-contact contributions leads in the general case to an improvement of the agreement between the theoretical and experimental values of $^1J_{CC}$, which is shown particularly for the $^{13}C-^{13}C$ SSCC for the triple bond.

The problem of the ratio of the contributions to the directly bonded $^{13}C-^{13}C$ SSCC has been studied thoroughly using a wide variety of non-empirical and semiempirical methods.[28–43]

In the general case the Fermi-contact contribution ($^1J^{Fc}$) is positive and as a rule predominates, the spin–orbital contribution ($^1J^{SO}$) is negative, and the dipole–dipole contribution ($^1J^{dd}$) has a variable sign and is insignificant. The non-contact interactions become significant for unsaturated and especially sterically strained systems with "unusual" hybridisation. In the latter, the role of the non-contact interactions increases mainly as a result of the decrease of the Fermi-contact contribution, which may be negative in the given instance.[44–48] For example, in the molecules of bicyclobutane (I) and benzvalene (II), a structural isomer of benzene, all three contributions to $^1J_{CC}$ by the bridging carbon atoms# are comparable in magnitude and negative,[44] i.e. the theory predicts in this case the negative sign of the resulting constant, which was subsequently confirmed experimentally.[49,50]



(I) (II)

Another extreme example is provided by acetylene derivatives in which all three contributions are positive.[26,39–41]

Table 1. The relative contributions of $^1J^{Fc}$, $^1J^{SO}$, and $^1J^{dd}$ (Hz) to the directly bonded $^{13}C-^{13}C$ SSCC for ethane, ethylene, and acetylene calculated using various methods.[26]

Method of calculation	H_3C-CH_3		$H_2C=CH_2$		$HC\equiv CH$	
	^1JFC	^1JSO + ^1Jdd	^1JFC	^1JSO + ^1Jdd	^1JFC	^1JSO + ^1Jdd
Non-empirical method with scanning of molecular orbitals	19.7	—	53.9	—	14.9	—
Non-empirical method involving direct summation with respect to states	17.4	0.6	69.2	—1.2	190.7	2.2
Non-empirical generalised Hartree–Fock method	—	1.2	—	—7.4	—	19.7
Method of finite perturbations in terms of the INDO approximation	41.5	—	82.1	—	163.8	—
Self-consistent theory of finite perturbations in terms of the INDO approximation	35.6	—2.2	70.6	—14.7	140.8	31.9
Method of finite perturbations in terms of the MINDO/3 approximation	29.9	0.2	72.3	2.5	84.0	87.5
Method involving direct summation with respect to states in terms of the INDO approximation with localised molecular orbitals	27.2	—1.1	71.6	—2.7	141.6	3.6
Experiment (Ref.2)	34.6		67.6		171.5	

It is noteworthy that the results of the study of the ratio of the contributions to $^1J_{CC}$ depend greatly on the computational methods employed, and they should therefore be interpreted with a certain amount of caution. Table 1 presents the values of the Fermi-contact contributions and the sums of the non-contact contributions ($^1J^{dd}$ + $^1J^{SO}$), calculated by several methods for ethane, ethylene, and acetylene molecules. Different methods yield a very significant scatter both in the estimates of the relative significance of the individual contributions and in the calculated $^1J_{CC}$, which is manifested particularly strikingly for the acetylene molecule. The method of finite perturbations in terms of the MINDO/3 approximation is apparently least applicable to the calculation of $^1J_{CC}$ for acetylenic compounds in view of the fact that the relative role of non-contact interactions is then found to be clearly too high.

Here and henceforth the asterisk denotes the interacting carbon nuclei.

2. The Types of Coupling

The three mechanisms of the coupling of the ^{13}C nuclear spins enumerated above can involve the participation of orbitals of the σ or π type. In order to separate these two types of coupling, the method of partly restricted and molecular orbitals was used in terms of the INDO approximation and it was shown that the Fermi-contact coupling takes place mainly via the σ system, while both types of non-contact coupling involve almost completely the π-electron system.[51] Using the method of direct summation with respect to states, it was established, in terms of the INDO approximation, that the spin–spin coupling between the ^{13}C nuclei linked directly in the acetylene, ethylene, and benzene molecules takes place via the σ mechanism.[52] A similar conclusion was reached as a result of the calculation of $^1J_{CC}$ for the same molecules by the method of the self-consistent theory of finite perturbations in terms of the INDO approximation with subsequent exclusion of the one-centre exchange integrals between the 2*s* orbital and one or more of selected 2*p* orbitals of one of the interacting carbon atoms.[53]

Thus, in the case where the Fermi-contact contribution predominates (which is the case in almost all compounds), the spin–spin coupling between carbon nuclei linked directly takes place via the σ-electron system.

III. THE PRINCIPAL FACTORS DETERMINING THE VARIATION OF THE DIRECTLY BONDED $^{13}C-^{13}C$ SSCC

1. Hybridisation of the Interacting Atoms

The main factor determining the variation of the directly bonded $^{13}C-^{13}C$ SSCC is the hybridisation of the interacting carbon atoms. In the very first experiment, it was already observed that the $^1J_{CC}$ increase sharply with increase of the amount of *s* character, i.e. the contribution by the 2*s* orbitals of the carbon atoms involved in the formation of the corresponding carbon–carbon bond.[1–3]

The observed variation becomes understandable if account is taken of the fact that the Fermi-contact contribution $^1J^{Fc}$ (which, as mentioned above, predominates in the vast majority of cases) is proportional to the *s* character of the bond in terms of the "average excitation energy" approximation:[27]

$$^1J^{Fc} = \frac{64\pi^2\beta^2}{9(\Delta E)}\langle s_A|\delta(r_A)|s_A\rangle\langle s_B|\delta(r_B)|s_B\rangle P^2_{s_As_B}. \quad (1)$$

where β is the Bohr magneton, ΔE the average excitation energy, $\langle s_A|\delta(r_A)|s_A\rangle$ and $\langle s_B|\delta(r_B)|s_B\rangle$ are the one-centre integrals for the 2*s* orbitals of the carbon atoms A and B, and $P_{s_As_B}$ is the corresponding first order density matrix of the valence *s* electrons.

(a) The Formal Relation with Hybridisation

The first quantitative description of the directly bonded $^{13}C-^{13}C$ SSCC in the context of the hybridisation of the interacting atoms was proposed by Frei and Bernstein, who measured $^1J_{CC}$ for thirteen ^{13}C-labelled compounds corresponding to six formal types of hybridisation of the interacting atom and established that the SSCC $^1J_{CC}$ (Hz) is proportional to the product of the *s* characters of the hybrid orbitals forming the corresponding carbon–carbon bond:[3]

$$^1J_{AB} = 576 s_A s_B - 3.4 \quad (2)$$

Later, an analogous relation was obtained by Günther and Herrig.[54]

A more accurate description of this relation was proposed by Newton et al.,[44] who observed a correlation between the experimental $^1J_{CC}$ (Hz) and the products of the *s* characters of the hybrid orbitals calculated by the method of finite perturbations in terms of the INDO approximation for sixteen hydrocarbons of different structure:

$$^1J_{AB} = 621 s_A s_B - 10.2 \quad (3)$$

The last relation differs from Eqn.(2) by a significant negative constant term, which is important, as will be shown below, for the description of the variation of $^1J_{CC}$ for sterically strained systems.

An attempt has been made[55] to include in the correlation equations of types (2) and (3) the overlap integral of the hybrid orbitals of the interacting atoms, but the relation obtained has not been widely used.

If it is assumed that the one-centre overlap integrals of the 2*s* orbitals of the carbon atoms in Eqn.(1) are constant, then, under conditions where the Fermi-contact interaction predominates, the SSCC $^1J_{CC}$ should be proportional to the square of the corresponding element of the density matrix $P^2_{s_As_B}$. Similar relations have been noted in other studies.[53,56,57] Recalculation of the data of Maciel et al.[53] by the method of least squares using the experimental values of $^1J_{CC}$ known at the present time led us§ to Eqn.(4) describing the variation of 60 values of $^1J_{CC}$ for 47 compounds with different hybridisation of the interacting atoms ($r = 0.956$, $s = 3.5$ Hz):

$$^1J_{AB} = 475.7\,(\pm 19.0)P^2_{s_As_B} + 6.6\,(\pm 1.8) \quad (4)$$

The description of the variation of $^1J_{CC}$ in the context of the hybridisation has been satisfactorily confirmed experimentally for various compounds,[54–56] including charged systems.[61]

(b) The Inadequacy of the Hybridisation Model

The successful description of the variation of $^1J_{CC}$ within the framework of the concept of hybridisation has become possible only for a set of systems with a wide variation of the *s* character of the bonds being compared and without substituents having markedly different electron-donating (electron-accepting) and steric properties. A number of examples are known where the hybridisation model does not reflect even the principal trend in the variation of $^1J_{CC}$.[62–66] There may be several reasons for the inadequate description in this instance.

The constant term in the correlation equations (2)–(4) corresponds to a constant overall contribution of the non-contact interactions independent of the *s* character of the bond.[30] Therefore the inconstancy of the non-contact interactions may introduce a significant error in the calculation of $^1J_{CC}$ by means of these equations, which applies in the first place to the spin–orbital contribution.

On the other hand, the effect of substituents, which is underestimated or, conversely, overestimated in the formal calculations of the amount of *s* character of the hybrid orbitals or the elements of the density matrix of the valence *s* electrons (different electronic and steric effects, the effect

§ L.B.Krividin, S.V.Zinchenko, V.V.Shcherbakov et al., Zhur.Org.Khim., 1987 (in the Press).

of unshared electron pairs of heteroatoms, etc.) can induce a significant variation of $^1J_{CC}$. For example, the range of variation of $^1J_{CC}$ for a triple bond, caused by the influence of substituents, is ~170 Hz (Fig.1).

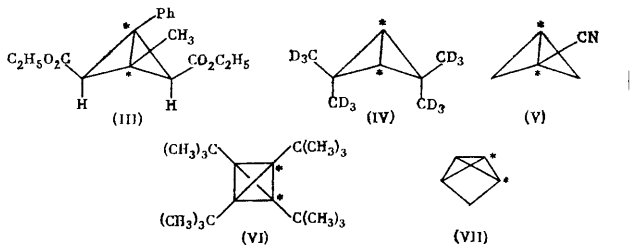
The correlation of $^1J_{CC}$ with various characteristics of the *s* character of the bond are based on the fairly rough (average excitation energy) approximation, which has been used to eliminate summation with respect to triplet states in the second-order perturbation theory.[33] The use of various quantum-chemical methods leads to an appreciable scatter of the *s* character of the bond, which also affects the overall quality of correlations of types (2)–(4). For example, the sum of the amounts of *s* character of the four equivalent hybrid orbitals of the central carbon atom of neopentane, calculated using the most accurate Eqn.(2), is 136%, i.e. it exceeds by 36% the maximum permissible value.[67]

The sterically strained mono-, di-, and poly-cycloalkanes—compounds with "unusual" hybridisation—constitute a special case. For example, the bond between the bridging carbon atoms in bicyclobutane is believed to be of the $sp^{2.4}$–$sp^{2.4}$ type (which corresponds to 4% of the *s* character of the hybrid orbitals forming the bridge bond).[68] The interest in the ^{13}C–^{13}C SSCC for these compounds is therefore understandable.[44–50,68–79]

On the basis of the simplest model of the structure of the cyclopropane ring, each carbon atom forms two exocyclic hybrid orbitals with 33% of *s* character of the sp^2 type and two endocyclic orbitals with 17% of *s* character, which corresponds approximation to sp^5 hybridisation. The use of the classical Frei–Bernstein equation [Eqn.(2)] leads to $^1J_{SS} \cong$ 16 Hz as the directly bonded ^{13}C–^{13}C SSCC between two ring carbon atoms of the cyclopropane ring,[70] which is close to the experimental value of 12.4 Hz.[47]

In the case of bicyclobutane, even the Frei–Bernstein equation predicts a negative value of the constant ($^1J_{CC} \cong$ −3 Hz) for the coupling between the bridging carbon atoms, while according to the more accurate Eqn.(5), the value in this case should be above −10 Hz.[44] As mentioned above, the same result follows also from the calculation of the three theoretical contributions to the given constant.[44,75]

The theoretical prediction of the negative sign of the directly bonded ^{13}C–^{13}C SSCC between the bridging carbon atoms in systems of the bicyclobutane type has been confirmed experimentally by Pomerantz and Finkelmeier, who carried out unique experiments involving the measurement of the signs of the ^{13}C–^{13}C SSCC for 1-methyl-[3-^{13}C]phenylbicyclo[1.1.0]butane-1,3-*exo*,*endo*-2,4-dicarboxylate (III) ($^1J_{CC}$ = −5.4 ± 0.5 Hz [49]) and 2,2,4,4-tetra(trideuteriomethyl)bicyclo[1.1.0][1,3-$^{13}C_2$]butane (IV) ($^1J_{CC}$ = −17.49 ± 0.2 Hz [50]). In the light of these data, the corresponding SSCC $^1J_{CC}$ for 1-cyanobicyclobutane (V) ($^1J_{CC}$ = 16.0 Hz [71,72]), tetra-t-butyltetrahedrane (VI) ($^1J_{CC}$ = 9.2 Hz [48]), and tricyclo[2.1.0.$0^{2,5}$]pentane (VII) ($^1J_{CC}$ = 19.0 Hz [76]) should also be regarded as negative.



As already mentioned, the hybridisation $^1J_{CC}$ model suffers from a number of limitations. In sterically strained systems, the limitation associated with failure to take into account the geminal (for three-membered rings) and vicinal (for four-membered rings) ^{13}C–^{13}C interactions, which involves independent pathways and lead to an additive contribution to the direct constant, assumes special importance.[30,47,48] For example, according to Stöcker's data,[47] the geminal interaction in cyclopropane leads to the contribution $^2J'_{CC}$ = −20.08 Hz, while the direct interaction leads to the contribution $^1J'_{CC}$ = 33.45 Hz, which results in the constant $^1J_{CC}$ = $^1J'_{CC}$ + $^2J'_{CC}$ = 12.47 Hz, agreeing exactly with the experimental value $^1J_{CC}$ = 12.4 Hz.[47] In the given interpretation, cyclopropane is a molecule with the "usual" sp^3 hybridisation.

Thus, in describing the variation of $^1J_{CC}$ within the framework of a simple hybridisation model, much care must be exercised in taking into account more secondary factors such as the electronic and steric effects of the substituents, the ratio of the contributions of the non-contact interactions in the series of compounds compared, and certain others.

2. Effects of Substitution

A factor of secondary importance, determining the variation of $^1J_{CC}$, is the electronic influence of substituents via the system of bond electrons (the steric effects of substituents will be considered separately). Derivatives of acetylene,[39,80–82] ethylene,[57,83–90] ethane,[56,91,92] benzene,[31,37,93–103] pyridine,[104] adamantane and diamantane,[106–108] and also, to a lesser extent, those of other compounds,[34,47,62,63,70,77,109–122] have been most thoroughly investigated in this sense. This Section deals with the general consideration of the effects of substitution without presenting extensive factual data; these data have been partly included in two compilations.[5,6]

(a) General Characteristics

The linear increase of $^1J_{CC}$ with increasing electronegativity of the first atom of the substituent (E_X)[37,39,88] or other characteristics reflecting its induction properties and acting via the system of σ-bonds of the molecule[81,94,95,123] has been noted in a series of studies of the influence of substituents on directly bonded ^{13}C–^{13}C SSCC. For example, for monosubstituted ethylene and acetylenes, these relations have the following form respectively:[39,88]

$$^1J_{CC} = 14.4E_X + 33.1 \quad (5)$$

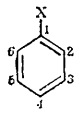
$$^1J_{CC} = 43.4E_X + 17.3 \quad (6)$$

According to the results obtained by the method of finite perturbations in terms of the INDO approximation, electronegative substituents X in the C–C–X fragment diminish the *s* character of the hybrid carbon orbital involved in the formation of the C–X σ-bond, which leads in its turn to an increase of the *s* character of the second hybrid orbital of the same carbon atom forming the C–C bond.[92] This increases the contribution of the Fermi contact interaction of the two carbon atoms considered and hence increases the constant $^1J_{CC}$, which is apparently a general principle for any system. These ideas have been confirmed by the results of calculations of ~70 values of $^1J_{CC}$ for more than 40 derivatives of ethane, ethylene, acetylene, and benzene by the self-consistent finite perturbation theory in terms of the INDO approximation.[32] According to the results of the last study quoted, the influence of substituents on $^1J_{CC}$ for a neighbouring carbon–carbon bond is exerted mainly as a result of the alteration of the Fermi-contact contribution to the ^{13}C–^{13}C SSCC.

The only known exceptions are cyclopropane derivatives in which the electronegative substituents CO_2H, CN, and COR (R = H or alkyl) decrease $^1J_{CC}$ compared with the unsubstituted cyclopropane; this may be explained by the interaction of the *p* orbitals of the α-carbon atom of the substituent with the "Walsh orbitals" of the cyclopropane ring, which decreases the *s* character of the endocyclic hybrid carbon orbital forming a carbon–carbon ring bond.[47] Account must also be taken of the fact that the spin–orbital interaction, sensitive to the redistribution of π-electron density,[51] makes a major contribution in the given instance to the ^{13}C–^{13}C constant.[44–48]

The influence of substituents on $^1J_{CC}$ decreases rapidly with increase in the number of intervening bonds separating the interacting atoms from the site of substitution.

For example, the ranges of the variation of $^1J_{CC}$ in the series of monosubstituted benzenes (VIII) are respectively Δ^1J_{CC} = 21.3 Hz, $\Delta^1J_{2,3}$ = 4.7 Hz, and $\Delta^1J_{3,4}$ = 1.9 Hz.[37]



(VIII)

An analogous relation is characteristic also of adamantane,[107] diamantane,[108] and pyridine[104] derivatives. The character of the dependence of $^1J_{CC}$ for the ^{13}C nuclei in the β- and γ-positions relative to the site of substitution on the electronegativity of the substituent may be directly opposite for different compounds.[37,104,107,108] It can be assumed that $^1J_{CC}$ for the even more remote bonds is almost insensitive to the influence of substituents transmitted via the system of σ-bond electrons.

A dependence of $^1J_{CC}$ on the π-electronic properties of substituents has been noted in some cases[31,38,47,93,96,99,100,101] but in most cases these effects are apparently associated with the π-induced redistributions of s-electron density, i.e. ultimately with the change in the *s* character of the bond.

The question of the additivity of the effects of substitution, which has so far been scarcely investigated, is extremely interesting for the practical application of $^1J_{CC}$ in structural studies. The additivity of the effects of substitution in the benzene rings of aromatic ethers and sulphides on $^1J_{CC}$, with the exception of instances of specific interaction of substituents in close proximity, has been noted.[124] The additivity of the influence of the phenyl group on $^1J_{CC}$ for the double bond has also been established.[38] A distinct non-additivity has been observed for the ^{13}C–^{13}C SSCC for the cyclopropane ring[47] and the triple bond.[80,125] For example, the experimental values of $^1J_{CC}$ for compounds (IX), (X) and (XI) exceed the values of this constant calculated using an additive scheme respectively by 10.2, 12.0 and 32.0 Hz:[125]

$(C_2H_5)_3Si{-}C{\equiv}C{-}Si(C_2H_5)_3$ (IX)

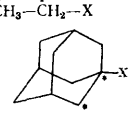
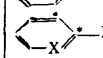
$(C_4H_9)_3Sn{-}C{\equiv}C{-}Sn(C_4H_9)_3$ (X)

$(CH_3)_3Sn{-}C{\equiv}C{-}Si(CH_3)_3$ (XI)

(b) Comparative Analysis of the Effects of Substitution

Table 2 gives a compilation of the increments Δ^1J_{CC} for the commonest substituents in certain model systems corresponding to different types of hybridisation of the interacting atoms. The Δ^1J_{CC} increase sharply with the increasing *s* character of the corresponding carbon–carbon bonds, which

Table 2. The substitutional increments in $^1J_{CC}$ (Hz) for the commonest substitutents[a].

Formal type of hybridisation	System	Substituents X										Refs.
		$Si(CH_3)_3$	CH_3	$COCH_3$	CO_2CH_3	CN	NH_2	Cl	Br	I	OCH_3	
sp^2–sp^2		—	+0.9	-2.2[b]	-2.6[c]	−1.5	—	+1.5	+0.9	+0.5	—	[47]
sp^3–sp^3	$\dot{C}H_3{-}\dot{C}H_2{-}X$	-2.8[d]	−1.6	+0.9	+0.2[c]	−1.6	+1.2	+1.5	+1.4	+1.2	+4.2	[56,92]
sp^3–sp^3		—	+0.3	−0.1	-0.3[c]	−0.1	+2.2	+1.7	+1.1	+0.7	+3.3[e]	[107]
sp^3–sp^2	$\dot{C}H_3{-}\dot{C}(=CH_2)X$	—	−0.1	—	+2.7	+3.0	—	+6.6	—	—	+9.9[f]	[57]
sp^3–sp^2	$\dot{C}H_3{-}\dot{C}(=O)X$	—	+0.7	—	—	—	+12.8[g]	+16.7	+14.7	+7.1	+19.4[f]	[62]
sp^2–sp^2	$H_2\dot{C}{=}\dot{C}H{-}X$	-8.2[h]	+2.4	—	+0.7	+3.0	+8.4[i]	+9.9	+8.7	—	+11.0	[5,88]
sp^2–sp^2		-6.5[k]	+1.1	+1.8	+2.3	+4.1	+5.1	+9.2	+7.7	+5.0	+11.1	[37,96]
sp^2–sp^2		—	+1.9	—	+5.3	+7.3	—	+13.1	+10.6	—	+16.4	[104]
sp–sp	$H\dot{C}{\equiv}\dot{C}{-}X$	−39.0	+0.4[l]	+8.4[m]	+7.3[c]	+24.1[m]	+7.5[o]	+23.7[m]	+21.3[m]	—	+58.4[p]	[39,81]

[a] $\Delta^1J_{CC} = {}^1J_{CC}(X) - {}^1J_{CC}(H)$. [b] For the substituent CO–  ; [c] For the substituent CO_2H. [d] For the substituent $SiH(C_2H_5)_2$. [e] For the substituent OH. [f] For the substituent OC_2H_5. [g] For the substituent $N(C_2H_5)_2$. [h] For the substituent $Si(CH_3)_2Cl$. [i] Estimated on the basis of an additive scheme for the substituent $N(C_2H_5)_2$. [k] For the substituent SiH_3. [l] For the substituent C_4H_9. [m] For the substituent $COCH(CH_3)_2$. [n] Estimated on the basis of an additive scheme. [o] Estimated on the basis of an additive scheme for the substitutent $N(CH_3)_2$. [p] Estimated on the basis of an additive scheme for the substituent 4-$CH_3C_6H_4O$.

also demonstrates the dependence, presented in Fig. 2 of the Δ^1J_{CC} for the substituents $Si(CH_3)_3$, $COCH_3$, CN, and OCH_3 on the product of the *s* characters of the interacting atoms. This is most notable when the values of $^1J_{CC}$ for the "strongest acting" substituents $Si(CH_3)_3$ and OCH_3, amounting to −40 and +60 Hz respectively for acetylene derivatives corresponding to the *sp*–*sp* hybridisation, are compared.

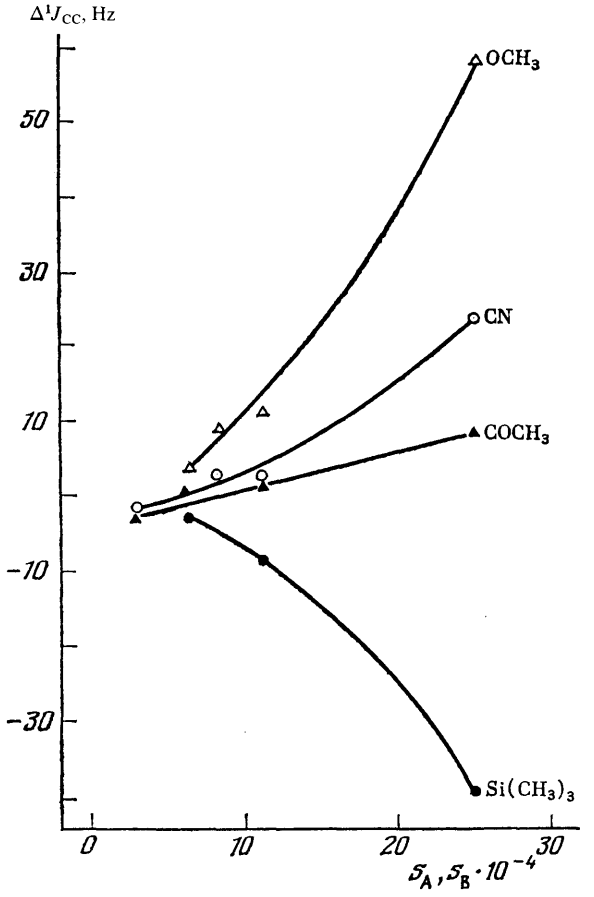


Figure 2. Variation of the increments Δ^1J_{CC} for certain substituents with the product of the amounts of *s* character of the interacting atoms.

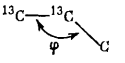
3. Steric Effects

The directly bonded $^{13}C-^{13}C$ SSCC are stereospecific with respect to the spatial distribution of individual structural fragments of the molecule, which makes it possible to use these parameters for the solution of a wide variety of stereochemical problems. The principal types of steric effects of substituents reflected in the values of $^1J_{CC}$ are briefly considered below.

(a) Effects Association with Changes in Valence Angles

The steric interactions of substituents are capable of inducing changes in molecular geometry leading to changes in the hybridisation of individual orbitals (which is determined in the first place by the bond angles) and hence to changes in the *s* characters of the bond and the corresponding $^{13}C-^{13}C$ SSCC. The first experimental manifestation of such effects has been observed in a study of $^1J_{CC}$ for ethane derivatives.[92] At first sight the unexpected increase in $^1J_{CC}$ on successive increase in the number of methyl groups at one of the interacting carbon atoms becomes understandable if account is taken of the fact that this leads to a gradual increase in the bond angle in the $^{13}C-^{13}C-CH_3$ fragment compared with the tetrahedral bond angle (by 5° [92]) and hence to an increase in the *s* character of its hybrid orbitals and correspondingly in the Fermi-contact contribution to the constant $^1J_{CC}$.

A quantitative description of this relation has been proposed by Pomerantz and Bittner,[126] who established that $^1J_{CC}$ for the fragment (XII) in a series of monohydrocarbons with a known geometry exhibits a quadratic dependence on the bond angle:



(XII)

$$^1J_{CC} = -0.00566\,\varphi^2 + 1.377\,\varphi - 49.04. \quad (7)$$

When ϕ is increased from 60° to 126.5°, $^1J_{CC}$ increases from 13.3 to 35.14 Hz.[126]

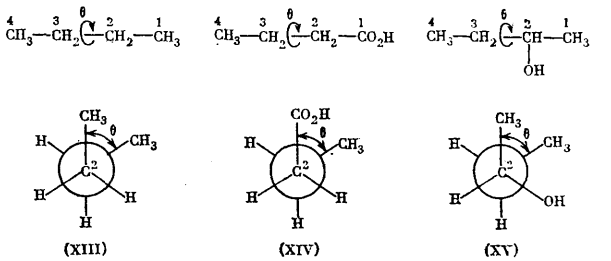
In a later study,[78] it was shown that, when cyclopropane, for which the observed $^1J_{CC}$ is the sum of the SSCC for two independent types of spin–spin coupling, is excluded from consideration, the observed dependence is linear:

$$^1J_{CC} = 0.166\,\varphi + 14.91 \quad (8)$$

Extrapolation of Eqn. (8) to ϕ = 60° leads to the "true" value of the directly bonded carbon–carbon constant for cyclopropane: $^1J_{CC} \cong 25$ Hz.[78]

(b) Effects Associated with Changes in the Mutual Orientation of the Bonds

Calculation of $^1J_{CC}$ by the method finite peturbations in terms of the INDO approximation for butane (XIII), butyric acid (XIV), and 2-butanol (XV) revealed a distinct stereospecificity of $^1J_{1,2}$ with respect to the mutual orientation of the C(1)–C(2) and C(3)–C(4) bonds, i.e. the dependence of $^1J_{CC}$ on the dihedral angle θ:[33]

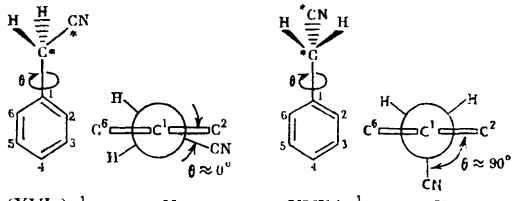


(XIII) (XIV) (XV)

The increase in θ from 0° to 180° reduces $^1J_{CC}$ by 4.5–6 Hz.

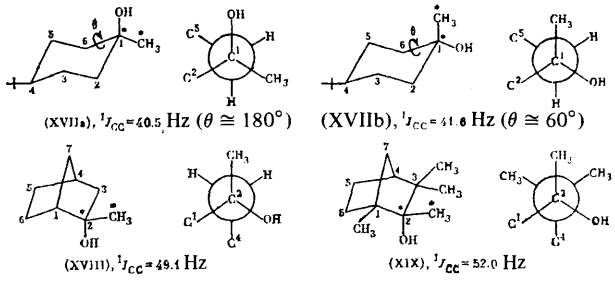
A difference between the theoretical values of $^1J_{CC}$ calculation was performed taking into account only the Fermi-contact contribution) for the planar and orthogonal conformers of benzyl cyanide (XVIa, b) has been noted.[127] This too can be explained by the change in the C(2)–C(1)–CH_2–CN

dihedral angle θ.



(XVIa), $^1J_{CC}$ = 76.3 Hz (XVIb), $^1J_{CC}$ = 75.0 Hz

The experimental values of $^1J_{CC}$ for *cis*- and *trans*-4-t-butyl-2-methylcyclohexanols (XVIIa, b), *exo*-2-methyl-2-norborneol (XVIII), and *exo*-2-methyl-2-fenchone (XIX) [33] reflect the same relation.

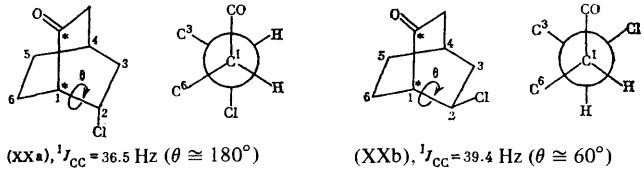


(XVIIa), $^1J_{CC}$ = 40.5 Hz ($\theta \cong 180°$) (XVIIb), $^1J_{CC}$ = 41.6 Hz ($\theta \cong 60°$)

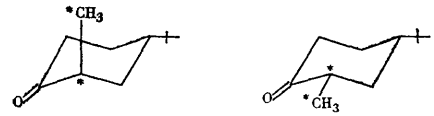
(XVIII), $^1J_{CC}$ = 49.1 Hz (XIX), $^1J_{CC}$ = 52.0 Hz

Analogous effects have also been noted in certain diamantane derivatives. [108]

The relation discussed above has also been observed in the $^{13}C-^{13}C-C-X$ fragment, where X is a heteroatom, as happens in the *exo*- and *endo*-derivatives of bicyclo[2.2.2]octanone (XXa, b) [128] and the pairs of 4-t-butyl-2-methyl-cyclohexanone diastereoisomers (XXIa, b). [129]



(XXa), $^1J_{CC}$ = 36.5 Hz ($\theta \cong 180°$) (XXb), $^1J_{CC}$ = 39.4 Hz ($\theta \cong 60°$)

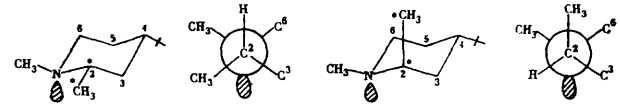


(XXIa), $^1J_{CC}$ = 33.8 Hz (XXIb), $^1J_{CC}$ = 37.6 Hz

The striking stereospecificity of $^1J_{CC}$ with respect to the orientation of neighbouring bonds makes it possible to employ these constants also for the solution of various problems in conformational analysis.

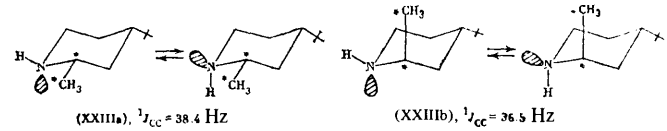
4. Effects of Unshared Electron Pairs of Heteroatoms

The stereospecificity of the directly bonded $^{13}C-^{13}C$ SSCC with respect to the orientation of the unshared electron pair of the nitrogen atom was first noted by Barna and Robinson for pairs of diastereoisomers of piperidine derivatives. [129] $^1J_{CC}$ for the *cis*-isomer of 4-t-butyl-2-*N*-dimethylpiperidine (XIIa) with the *gauche*-disposition of the C(2)–CH_3 bond and the unshared electron pair of the nitrogen atom is greater by 4 Hz than the corresponding constant for the *trans*-isomer (XXIIb):



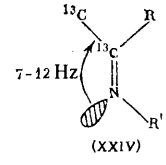
(XXIIa), $^1J_{CC}$ = 39.3 Hz (XXIIIb), $^1J_{CC}$ = 35.3 Hz

The difference between the constants for the corresponding NH derivatives is reduced to ~2 Hz as a consequence of the shift of the conformational equilibrium of the *trans*-isomer (XXIIIb) towards the form with the *gauche*-orientation of the unshared electron pair and of the carbon–carbon bond considered:



(XXIIIa), $^1J_{CC}$ = 38.4 Hz (XXIIIb), $^1J_{CC}$ = 36.5 Hz

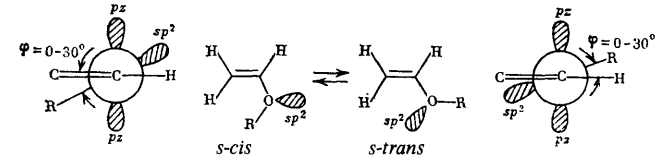
The effect of the unshared pair of the imino-nitrogen, leading to an additional contribution to $^1J_{CC}$ for the neighbouring carbon–carbon bond of the fragment (XXIV), amounting to up to 12 Hz, which permits an unambiguous identification of the configurations of a wide variety of imines, has been noted in a series of studies. [123,130–135]



(XXIV)

An analogous influence of unshared electron pairs has also been established for a series of oxygen-containing compounds. [90,124,136,137]

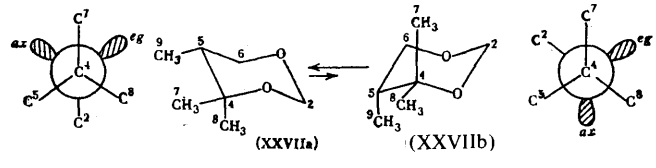
The shift of the conformational equilibrium in a series of alkyl vinyl ethers towards the *s-trans*-conformer with the *cis*-orientation of the sp^2-hybridised unshared electron pair of oxygen with respect to the double bond leads to an additional contribution to the corresponding $^{13}C-^{13}C$ constant up to ~4 Hz: [136]



s-cis *s-trans*

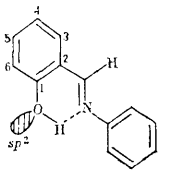
R = CH_3 (XXV), $^1J_{CC}$ = 78.6 Hz; R = $C(CH_3)_3$ (XXVI), $^1J_{CC}$ = 82.2 Hz

The same effect has been observed also for the sp^3-hybridised unshared electron pairs of the oxygen atom of 4,4,5-trimethyl-1,3-dioxan (XXVII). [137] The equilibrium in this compound is displaced towards the conformer (XXVIIa). The constant $^1J_{4,7}$ exceeds $^1J_{4,8}$ by ~3.5 Hz owing to the additional contribution to the former by the axial sp^3-hybridised unshared pair of the neighbouring oxygen atom in the preferred conformer (XXVIIa), while the contributions of the equatorial unshared electron pair to the two constants are the same.



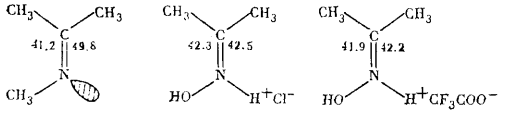
(XXVIIa) (XXVIIb)

According to Krivdin et al.,[124] the contribution of the hybridised unshared pair of the oxygen of the hydroxy-group in compound (XXVIII), rigidly fixed in the *cis*-position with respect to the C(1)–C(6) bond as a consequence of the formation of a strong intramolecular hydrogen bond, is ~7 Hz, which is comparable to the contribution by the unshared electron pair of the imino-nitrogen.



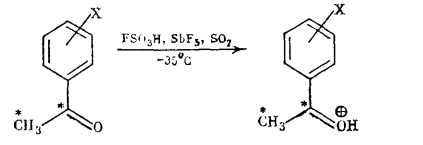
(XXVIII)

In view of the practical importance of the effects considered in stereochemical studies on heteroatomic compounds, the elucidation of the nature of the influence of the unshared electron pairs of the heteroatoms on the $^{13}C-^{13}C$ SSCC is of great interest. In their first study,[129] Barna and Robinson suggested that the observed effect is caused by the steric overlapping of the unshared electron pair of the heteroatom with the antibonding orbitals of the neighbouring C–C bonds, which increases $^1J_{CC}$ for the *cis*- and *gauche*-orientations and decreases this constant for the *trans*-orientation of the unshared pair and of the corresponding bonds.[129] However, the results for the protonation of the acetoxime (XXIX) support the view that the unshared electron pairs of the heteroatoms give rise to an additional contribution to the $^1J_{CC}$ for the neighbouring bond in the *cis*-position and hardly influences the $^1J_{CC}$ for the bond having the *trans*-orientation.[138] The constants $^1J_{CC}$ (Hz) for acetoxime (XXIX) and its protonated forms (XXIXa, b) are presented below.[138] They demonstrate unambiguously that the positive contribution to $^1J_{CC}$ for the neighbouring bond having the *cis*-orientation is in fact "removed" on protonation of the unshared electron pair.



(XXIX) (XXIXa) (XXIXb)

The "unexpected" decrease in $^1J_{CC}$ by ~5 Hz on protonation of the carbonyl oxygen in substituted acetophenones (XXX) with formation of the stable oxonium ions (XXXI)¶ [100] should also be apparently explained by the removal of the additional positive contribution of the unshared electron pair of the carbonyl oxygen to the corresponding constant.



(XXX), $^1J_{CC}$ = 43–44 Hz (XXXI), $^1J_{CC}$ = 38–40 Hz

So far nothing is known about the influence of the unshared electron pairs of other heteroatoms on the directly bonded $^{13}C-^{13}C$ SSCC. According to our own preliminary data,† one can assume that the effect under discussion is insignificant for the halogens, sulphur, and phosphorus.

5. Effects of the Medium

The effects of the medium are manifested in the variation of three main contributions to the direct SSCC caused by the influence of the solvent: the magnetic shielding induced by the magnetic moments of neighbouring molecules, dispersion effects of the exchange type, and intermolecular electrostatic interactions.[139] In the absence of specific solvation effects, the theory predicts the variation of the directly bonded SSCC for the two interacting A and B nuclei as a function of the dielectric constant of the solvent ε in accordance with Eqn.(9), which reflects mainly the variation of the contribution by the intermolecular electrostatic interactions:[140]

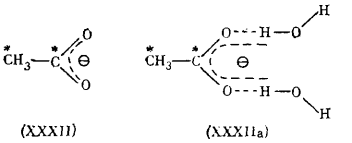
$$^1J_{AB} = a\left(\frac{\varepsilon-1}{\varepsilon}\right)^2 + b\left(\frac{\varepsilon-1}{\varepsilon}\right) + c \qquad (9)$$

However, the changes in the experimental values of $^1J_{CC}$ are comparable to the accuracy of the measurement of the constants even for a wide range of variation of the polarity of the medium.[34,80,123,141,142]

The few measurements of the temperature dependence of $^1J_{CC}$ indicate a low sensitivity of the $^{13}C-^{13}C$ SSCC to temperature.[39,123,142] For example, the constants $^1J_{CC}$ for a series of halogeno-derivatives of ethane, acetonitrile, and acetic acid increase by only 0.1–0.3 Hz when the temperature is raised by 100 °C.[142] The constants $^1J_{CC}$ are almost independence of the concentrations of the test compounds.[123]

The weak sensitivity of the $^1J_{CC}$ to solvation effects permits a correction comparison of the constants measured under different experimental conditions and, what is particularly important, in different solvents.

Like the conformational changes in the molecules induced by the solvent, in individual instances the specific associative processes may induce very large changes in the $^{13}C-^{13}C$ SSCC. For example, the calculated constants $^1J_{CC}$ for the acetate anion (XXXII) and its solvated form (XXXIIa) differ by ~35 Hz:[53]



(XXXII) (XXXIIa)

IV. STRUCTURAL APPLICATIONS

1. The Nature of the Carbon–Carbon Bonds and the Properties of Substituents

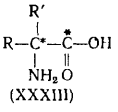
The direct $^{13}C-^{13}C$ SSCC can be used to estimate the hybridisation of individual atoms, and *s* characters of the bonds, and the *s* characters of individual orbitals and also

¶ In superacid media at −35 °C.

† L.B.Krivdin, V.V.Shcerbakov, and G.A.Kalabin, "Konstanty Spin–Spin Vzaimodeistviya $^{13}C-^{13}C$ Geteroatomnykh Soedinenii" (The $^{13}C-^{13}C$ Spin–Spin Coupling Constants for Heteroatomic Compounds) (Edited by V.A.Koptyug et al.), NIOKh Sibir.Otd.Akad.Nauk SSSR, Novosibirsk, 1988 (in the Press).

to refine the distribution of *s* electron density on carbon nuclei. The values of $^1J_{CC}$ are also reflected by the product of "empirical factors",[143] including the elements of the relative *s*-electron density, the C–C bond order, and the singlet–triplet excitation energy. A dependence of $^1J_{CC}$ on the π-bond order calculated by the Hückel method has been noted for a series of condensed aromatic hydrocarbons.[38,105,116,120]

On the other hand, the dependence of $^1J_{CC}$ on the *s* electron density and the weak sensitivity to π-electronic effects permit a wide-scale use of these parameters in the study of the induction properties of substituents in various systems.[37,39,81,88,94,95,123] One of the practical applications of such relations is in the method for the determination of the pK_a for carboxy-groups based on the dependence of $^1J_{CC}$ for the interaction of the carboxy-carbon atom with the neighbouring α-carbon atom in aminoacids (XXIII) on the degree of ionisation of the carboxy-group:[144–148]


(XXXIII)

On passing from an acid to a neutral medium, $^1J_{CC}$ for aminoacids diminishes by ~6 Hz; a further increase in pH, accompanied by a transition of the carboxy-group from the zwitterionic state to the anionic state, leads to a successive decrease in $^1J_{CC}$ by ~1 Hz.[145] The relation under discussion provides a unique possibility for the selective titration of individual amide groups in natural and synthetic peptides labelled with the ^{13}C isotope and for the determination of the degree of their ionisation in the active centres of enzymes.

The relation between $^1J_{CC}$ and the internuclear distances r_{CC} (Å) is of great interest. Eqn.(10) for the hybridisation of the interacting sp^3–sp^3, sp^3–sp^2, and sp^2–sp^2 atoms and Eqn.(11) for sp^3–sp, sp^2–sp, and sp–sp can be fitted to the available data:[54]

$$^1J_{CC} = -167r_{CC} + 294 \quad (10)$$

$$^1J_{CC} = -571r_{CC} + 855 \quad (11)$$

Eqns.(10) and (11) reflect the general trend involving a decrease of $^1J_{CC}$ with increase of the distance between the interacting atoms and can be used solely for rough estimates of r_{CC}.

More accurate equations have been obtained for a narrow range of condensed aromatic hydrocarbons, naphthalene, anthracene, phenanthrene, pyrene, and benzo[a]pyrene:[149]

$$^1J_{CC} = -143r_{CC} + 257 \quad (12)$$

$$^1J_{CC} = -119r_{CC} + 227 \quad (13)$$

Eqn.(12) corresponds to the case of the interaction of the methylidyne and quaternary ^{13}C nuclei, whilst Eqn.(13) corresponds to two methylidyne carbon nuclei.

The directly bonded dipole–dipole ^{13}C–^{13}C SSCC for partly oriented molecules in the nematic phase contain a large contribution due to the anisotropy of indirectly bonded carbon–carbon constants and their use for the determination of the internuclear distances r_{CC} is therefore limited.[150]

A study of the relaxation of the ^{13}C satellites in the carbon spectrum of phenylacetylene established that the ratio of the relaxation times for the pairs of satellites being compared corresponds exactly to the theoretical ratio of the dipole–dipole contributions to relaxation, which are proportional to r_{CC}^{-6}.[151] Thus the relaxation times of the ^{13}C satellites can also be used to estimate bond lengths.

A correlation between $^1J_{CC}$ and the bond force constants K_{CC}, whose experimental measurement is frequently difficult, has been observed.[152,153] The form of the equations depends on the hybridisation of the interacting atoms:

$$sp^3 - sp^3: K_{CC} = 0.0344\,^1J_{CC} + 3.25 \quad (14)$$

$$sp^2 - sp^2: K_{CC} = 0.1800\,^1J_{CC} - 3.25 \quad (15)$$

$$sp - sp: K_{CC} = 0.0295\,^1J_{CC} + 11.04 \quad (16)$$

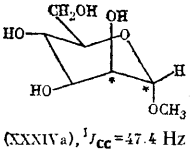
The use of these equations made it possible to define the bond force constants for a series of compounds, including epoxyethane, propene, butadiene, and diacetylene.[152]

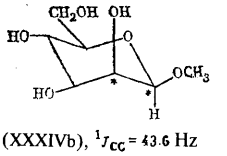
The directly bonded ^{13}C–^{13}C SSCC made it possible to expand significantly the ideas about the nature of the carbon–carbon coordinate bonds in transition and non-transition metal complexes.[154–157] In particular, it has been established that, in a series of allyl complexes, there is a strong "reverse donation" from the highest occupied molecular orbits of the ligand to the unoccupied orbitals of the metal, which is manifested by a sharp decrease of the constant $^1J_{CC}$ for the bonds in the ligand.[156]

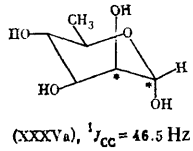
2. Stereochemical Studies

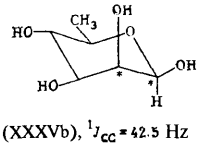
The marked stereospecificity of the directly bonded ^{13}C–^{13}C SSCC gives rise to major prospects for the use of these parameters in stereochemistry and conformational analysis. A series of problems associated with the steric orientation of the unshared electron pairs of heteroatoms have been solved with the aid of the ^{13}C–^{13}C SSCC: a new universal method has been developed for the determination of the configurations of compounds with imino-nitrogen;[123] the conformational analysis of a wide range of unsaturated and aromatic ethers and sulphides has been carried out;[90] a new method has been proposed for the identification of azole isomers;[158] the steric structure of pyrazolines—the products of the incomplete reduction of pyrazoles—has been studied.[159]

The directly bonded ^{13}C–^{13}C SSCC have found extensive applications in the stereochemistry of biologically important carbohydrates.[160,161] The constants $^1J_{CC}$ are presented as an example for methyl α- and methyl β-D-mannopyranosides (XXXIVa, b) and α-L- and β-L-rhamnoses (XXXVa, b). Here the constants are stereospecific with respect to the orientation of the substituent (OH, OCH_3) at C(1) and can thus be used to determine the steric structure of related glycosides and free sugars:[161]


(XXXIVa), $^1J_{CC}$ = 47.4 Hz

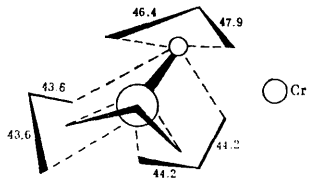

(XXXIVb), $^1J_{CC}$ = 43.6 Hz


(XXXVa), $^1J_{CC}$ = 46.5 Hz


(XXXVb), $^1J_{CC}$ = 42.5 Hz

In the studies of Benn and Rufinska,[155,156] the constants $^1J_{CC}$ were used to investigate the stereochemistry of allyl complexes of metals. For example, the measurement of $^1J_{CC}$ (Hz) for the dinuclear chromium complex (XXXVI) makes it possible to determine unambiguously the bridging η^3-allyl

groups, for which the values of $^1J_{CC}$ are significantly smaller:

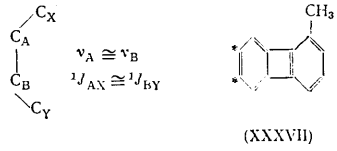


(XXXVI)

Thus the application of the directly bonded $^{13}C-^{13}C$ SSCC to the solution of a wide variety of stereochemical problems has led to the creation of a new promising method for the determination of the conformation and configurational structures of molecules.

3. Tracing Out the Carbon Skeleton of Complex Molecules

A universal method for the assignment of the ^{13}C NMR signals, which has come to be called "tracing out the carbon skeleton" has been developed using the directly bonded $^{13}C-^{13}C$ SSCC.[162] In the two-dimensional version of INADEQUATE, the carbon skeleton of the molecules is traced out by observing the two-quantum frequencies in the dimension $\mathcal{F}_1$ to which the usual carbon spectrum with ^{13}C satellites corresponds in the dimension $\mathcal{F}_2$; the ^{13}C nuclei linked directly are then readily identified from the identical two-quantum frequencies.[162] The use of this method is especially effective when the chemical shifts of the interacting nuclei are almost identical and the constants for their interaction with the neighbouring carbon nuclei are so close that they cannot be distinguished to within the accuracy of the experimental measurement, as happens, for example, in 1-methylbiphenylene (XXXVII):[163]



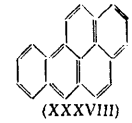
(XXXVII)

Despite the advantages noted above, when the two-dimensional version of INADEQUATE is used, two difficulties are encountered: the extremely acute problem of sensitivity, which frequently cannot be overcome even in the most sophisticated NMR spectrometers (in order to record a single two-dimensional INADEQUATE spectrum, it is necessary to obtain at least ~1000 ^{13}C satellite carbon spectra) and, on the other hand, the low numerical resolution in the transformed spectra which precludes the measurement of $^1J_{CC}$ with the necessary accuracy.

The alternative one-dimensional version of the INADEQUATE method is free from the above disadvantages. In this method, the carbon skeleton is traced out by identifying the carbon–carbon bonds as a result of the successive comparison of the values of $^1J_{CC}$ measured for each signal in the ^{13}C NMR spectrum. The COSMIC [164] and CABSA [165] programs ensure the complete automation of such an experiment.

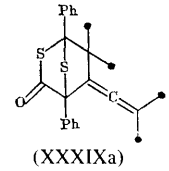
In the case of a high spectral signal density, the use of the DOUBTFUL pulse sequence[166] makes it possible to achieve an unambiguous assignment of the quaternary signals under INADEQUATE conditions with their preliminary filtration.

The method discussed is used widely for the assignment of the ^{13}C signals for complex organic compounds containing up to 40 carbon atoms. In a number of instances, the signals have been reassigned.[149,167–177] For example, the application of this method resulted in the reassignment of 11 out of the 20 ^{13}C NMR signals of the benzo[*a*]pyrene (XXXVIII) molecule.[149]

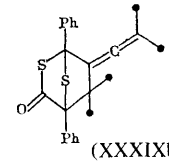


(XXXVIII)

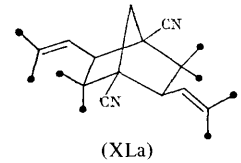
The isomers (XXXIXa, b),[178] (XLa, b),[179] and (XLIa, b),[180] which have very similar structures and cannot be distinguished on the basis of the ^{13}C NMR spectra, have been identified with the aid of this method.



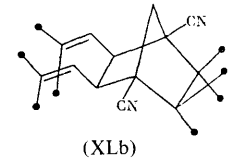
(XXXIXa)



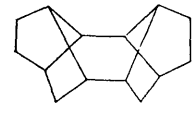
(XXXIXb)



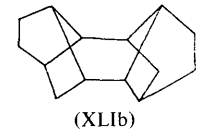
(XLa)



(XLb)

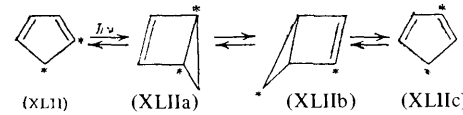


(XLIa)



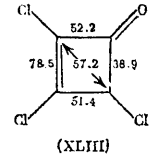
(XLIb)

The method for tracing out the carbon skeleton has already found application in the determination of the reaction mechanisms and for the identification of the intermediates.[76,181,182] An elegant example of studies of this kind is the determination of the pathway followed in the photoisomerisation of [1,2-$^{13}C_2$]cyclopentadiene (XLII):[76]

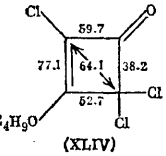


(XLII) (XLIIa) (XLIIb) (XLIIc)

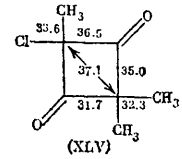
The unusually high values (tentatively positive) of the geminal constants $^2J_{CC}$ for the polychloro-derivatives of cyclobutenone and cyclobutanedione (XLIII)–(XLV), which can reach and actually exceed the values of $^1J_{CC}$, constitute a serious obstacle to the use of the method:[183]



(XLIII)



(XLIV)



(XLV)

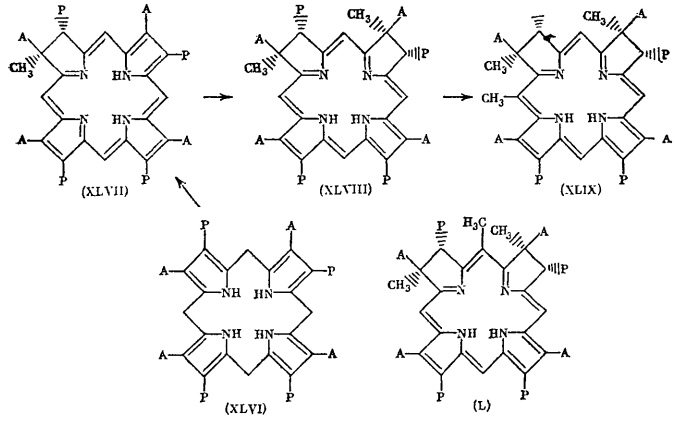
The two-dimensional version of the method discussed can be used to assign the repeating structural fragments in polymers without measuring the constants $^1J_{CC}$. The principal structural units (guaiacyl, syringyl, and pinoresinol) of the natural polymer lignin have been unambiguously assigned in this way.[184]

Thus, the method for tracing out the carbon skeleton is one of the most promising and rapidly developing applications of the direct $^{13}C-^{13}C$ SSCC in structural studies.

4. Determination of Biosynthetic Pathways

Directly bonded $^{13}C-^{13}C$ SSCC are widely used to determine the biosynthetic pathways for complex natural products.[9,185,186] The selective introduction of the ^{13}C isotope into the precursor molecule not only makes it possible to trace by the NMR method the fate of an individual atom as it passes through a sequence of biochemical reactions *in vivo* but also to determine unambiguously the site where ^{13}C is incorporated and to establish the structure of the compounds formed by the method for tracing out the carbon skeleton.

For example, the use of directly bonded $^{13}C-^{13}C$ SSCC makes it possible to establish, in the biosynthesis of vitamin B_{12}, the chain of successive transformations of intermediate precursors—sirohydrochlorin (XLVIII)—urogen-III (XLVI) derivatives.[187,188] The structure (L) had been attributed earlier erroneously to compound (XLIX).



The majority of studies concerning the use of $^1J_{CC}$ for the determination of biosynthetic pathways were based on the investigation of microbial metabolites enriched in [1,2-$^{13}C_2$]-acetate in the biosynthetic process. The earliest example of such investigations dates back to 1973: the incorporation of [1,2-$^{13}C_2$]acetate in dihydrolatumcidin.[189] The principles underlying the above study are widely used nowadays. In connection with the devlopment of the methods of synthesis of compounds enriched in the ^{13}C isotope, the most varied ^{13}C-labelled precursors, such as, for example, [U-$^{13}C_6$]-D-glucose,[190] [3,5-$^{13}C_2$]-L-tyrosine and [1,2-$^{13}C_2$]glycine,[191] [4,5-$^{13}C_2$]lysine,[192] [3,4-$^{13}C_2$]glutamate,[193] [1,2-$^{13}C_2$]propionate,[194] [2,3-$^{13}C_2$]succinate,[195,196] [5,6-$^{13}C_2$]nicotinic acid,[197,198] and certain others[199,200] have been used with increasing frequency in recent years.

The structures of about 300 most important products of the metabolism of animals and plants—polyketides, mixed metabolites, terpenes and steroids, aminoacids, and amino-acid metabolites—have now been determined with the aid of the $^1J_{CC}$ constants.

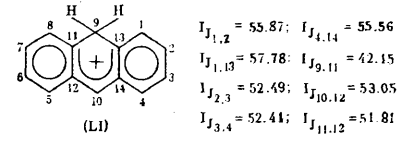
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During the preparation of the manuscript for printing, a number of studies dealing with the improvement of methodological procedures for the experimental measurement of $^{13}C-^{13}C$ SSCC, relating to problems of increasing the sensitivity of the basic INADEQUATE method in its one-dimensional and two-dimensional versions, the compensation for non-resonance effects, the development of new pulse sequences, and also for the elucidation of the possibility of measuring directly bonded $^{13}C-^{13}C$ dipole–dipole SSCC in the ^{13}C NMR spectra of solids have been published.[201–208]

The studies of the stereospecificity of the $^{13}C-^{13}C$ SSCC with respect to the orientation of the unshared electron pairs of heteroatoms (nitrogen[209,210] and oxygen[211–213]) have continued. The new experimental data confirm the conclusion that the additional contributions of the unshared pairs of these heteroatoms to the $^{13}C-^{13}C$ SSCC for neighbouring bonds are positive.

The structures of α-longipinene (a sesquiterpene),[214] the product of the cyclisation of the sesquiterpene hydrocarbon caryophyllene,[215] 1-methoxy-*endo*-tetracyclo[6.3.0.$0^{2,11}$.$0^{3,7}$]-undec-9-ene—the product of the photochemical cycloaddition of anisole to cyclopentene,[216] and the complex condensed heterocycle benzo[*b*]phenanthro[4,3-*d*]thiophen have been determined using the methods for tracing out the carbon skeleton, and their signals in the ^{13}C NMR spectra have been fully assigned.

There has been significant progress in studies on the $^{13}C-^{13}C$ SSCC for charged systems—carbonium ions of the bis-homotropylium type,[218] α-cyanodiaryl- and 1,1-diaryl-2-butynyl cations,[219] and also six-membered heteroatomic cations—the pyrylium, thiapyrylium, and seleninium ions.[220] In the last study,[220] the fundamental conclusion was reached that the lower values of $^1J_{CC}$ for positively charged systems compared with their neutral analogues can be accounted for by charge polarisation. This conclusion has been confirmed by the results of a unique experiment involving the measurement of $^1J_{CC}$ (Hz) for the anthracenium cation (LI) with the natural isotopic abundance.[221]



Progess has been noted in the theoretical study of $^{13}C-^{13}C$ SSCC. In this connection, special mention should be made of the study of Fronzoni and Galasso concerning the use of the non-empirical *ab initio* method to calculate $^1J_{CC}$ for monoheterocyclopropanes and cyclopropenes.[222] The work on the creation of a set of quantum-chemical programs IPPP RPA INDO (Inner Projections of the Polarisation Propagator at the Random Phase Approximation level using the INDO method), which makes it possible to investigate the mechanisms of the transfer of individual contributions to $^{13}C-^{13}C$ SSCC (fermi-contact, spin–orbital, and dipole–dipole) via bonds, individual molecular orbitals (including antibonding orbitals), and unshared electron pairs of heteroatoms is being completed.[223]

The work on the compilation of extensive experimental data has been completed and a survey of $^{13}C-^{13}C$ SSCC for the triple bond in a series of organoelemental and heteroatomic derivatives of acetylene is being prepared for printing.[224] Directly bonded $^{13}C-^{13}C$ SSCC have been used[225–232] for the solution of specific structural problems in the chemistry of saturated and carbocyclic, unsaturated, and aromatic, as well as heterocyclic compounds having different structures.

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Metal Carbonyl Catalysts of the Synthesis of Organic Compounds from Carbon Monoxide and Molecular Hydrogen

A.L.Lapidus and M.M.Savel'ev

Studies on the synthesis of organic compounds from carbon monoxide and hydrogen in the presence of catalysts obtained by the thermal decomposition of metal carbonyls on inorganic carriers are examined. The characteristic features of the interaction of various metal carbonyls with the carriers and the mechanisms of the formation of the metal carbonyl catalysts are discussed. The bibliography includes 165 references.

CONTENTS

I. Introduction 17
II. The interaction of metal carbonyls with the surfaces of carriers 17
III. Synthesis of organic compounds from CO and H_2 in the presence of metal carbonyl catalysts 22
IV. Conclusion 25

I. INTRODUCTION

The catalytic syntheses based on carbon monoxide and hydrogen constitute the basis of industrial methods of preparation of hydrocarbons and also of a number of oxygen-containing products. A vigorous search for active and selective catalysts capable of effecting these promising processes, which make it possible to obtain valuable compounds, including the components of motor fuels based on a non-petroleum raw material, is being vigorously prosecuted at the present time in our country and abroad.[1]

A new trend in this field involves the application of catalysts based on metal carbonyls. These catalysts can be divided into three main groups: the metal carbonyl systems proper, usually employed under the conditions of homogeneous catalysis, heterogenised complexes of transition metals, and catalysts obtained by depositing metal carbonyls on carriers with their subsequent decomposition. The application of catalysts of the first two types in the synthesis of hydrocarbons from CO and H_2 has been described in detail by the present authors[2] and their application in the synthesis of oxygen-containing compounds has been described by Dombek.[3]

The present review deals with catalysts of the synthesis of organic compounds from CO to H_2 obtained by decomposing metal carbonyls deposited on various carriers. The first studies on these lines were carried out 8–10 years ago. The number of publications devoted to this problem has continuously increased in recent years.

II. THE INTERACTION OF METAL CARBONYLS WITH THE SURFACES OF CARRIERS

The decomposition reactions of metal carbonyls on carriers and the catalyst formation reactions have been examined in a review.[4] Certain data concerning the mechanism of the interaction of metal carbonyls with inorganic carriers and also the catalytic properties of systems obtained by decomposing deposited metal carbonyls have been published.[4-6]

Inorganic carriers such as Al_2O_3, SiO_2, MgO, TiO_2, aluminosilicates, and zeolites are normally used to prepare the metal carbonyl catalysts. In certain cases the surfaces of the carriers are modified by functional groups (NR_2, PR_2, etc.) which are capable of being coordinated to the transition metal.

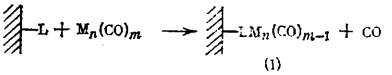
Two methods of synthesis of metal carbonyl catalysts are most widely used.[4] The first is based on the impregnation of the carrier with a solution of the carbonyl complex, usually in an organic solvent, with subsequent drying of the catalyst. In this case it is possible to obtain catalysts with any metal content, but at a high metal concentration the structures of the surface complexes obtained are as a rule inhomogeneous.

The second method is based on the adsorption of the metal carbonyl on the surface of the carrier from the gas phase or an organic solvent. Here the maximum content of the transition metal in the catalyst is determined by the adsorption capacity of the surface of the carrier used. In this instance the structure of the surface complex formed is more homogeneous.

Both methods of synthesis of the metal carbonyl catalysts are fairly universal and can be employed for virtually any types of carbonyl complexes as well as carriers.

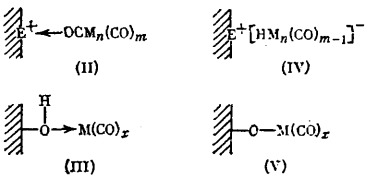
In a general form, the interaction of carbonyl complexes with the carrier surface can be described by the following schemes.[7]

(1) The substitution of CO or another ligand in the coordination sphere of the carbonyl complex by a functional group of the modified carrier:



(I)

(2) The interaction of the carbonyl complex with Lewis (E^+) or Brønsted centres on the surface of the unmodified oxide carrier with formation of various immobilised complexes:



(II) (IV) (III) (V)

Account must be taken of the fact that the interaction of the complexes with the carrier surfaces is described only approximately by the schemes presented above. The carbonyl complexes of transition metals readily react with acid or basic agents and the carrier surfaces as a rule contain a wide range of the corresponding functional groups. There is therefore a possibility of the parallel chemisorption of metal carbonyls on various surface centres with formation of several types of structures.

The interaction with a carrier may be accompanied by the decomposition of the carbonyl cluster or, conversely, by the formation of polynuclear cluster structures from mononuclear complexes. The occurrence of such processes greatly complicates the selective preparation of complexes of a specific type fixed on the carrier surface.

It must be emphasised that the direct interaction of the complexes with the active centres on the surface is of decisive importance only when the number of molecules of the carbonyl complex is comparable to the number of chemisorption centres on the carrier surface, i.e. virtually only for "low percentage" deposited metal catalysts. Otherwise the process is complicated still further as a consequence of the physical absorption of the carbonyl complexes on the outer surface and in particular within the carrier pores.

It is known[6] that the number and ratio of the Lewis and Brønsted centres on the surfaces of inorganic carriers depends greatly on the conditions of their preliminary treatment. Therefore, depending on the methods of preparation from the same initial reagents, it is possible to obtain catalysts having a different structure of the surface carbonyl complexes. IR spectroscopy is usually employed together with other physicochemical methods to investigate the mechanism of the interaction of carbonyl complexes with carriers and also the structures of the surface complexes produced.[4,6]

Account must be taken of the fact that the catalytic properties of the given systems have been studied to the greatest extent in reactions at temperatures below 200 °C (hydrogenation, isomersation, metathesis of olefins, etc.), for which a partial or complete decompostion of the surface carbonyl complexes does not occur. On the other hand, the syntheses of organic compounds from CO and H_2 normally require the application of higher temperatures. Therefore, after the deposition of the metal carbonyl on the carrier, the catalyst is in this case subjected to a preliminary heat treatment (*in vacuo* or in an atmosphere of CO, H_2, He, or a mixture of gases) in order to carry out a complete or partial decomposition of the complex and to form deposited metal particles (in an oxidised or reduced state). However, we may note that the carbonyls decompose also in the initial stages of the synthesis of CO and H_2 directly in the atmosphere of the synthesis gas.

1. Group VI Metal Carbonyls

The thermal decomposition of Group VI metal carbonyls has been investigated[9–31]) on various inorganic carriers by IR,[9–11,14,17,19,25,26,30] EPR,[10–12,19,21,22,27,28] NMR,[18] and XPE† spectroscopy[15] and by the thermoprogrammed decomposition method[13,16,20,21,23,31] (Table 1). The formation on chemisorption of the carbonyls of the surface complexes $M(CO)_5$ (ads), which exist at 20–40 °C [structure (III)][9,10] may be included among the general features of the given process. At temperatures of about 100 °C, the subcarbonyl species $M(CO)_3$(ads) are formed on the Al_2O_3 surface from molybdenum and tungsten carbonyls.[10,18–21] Such complexes have not been observed on the SiO_2 surface.[13] It has been suggested[14] that the stability of the subcarbonyl species increases with decrease in the acidity of the surface OH groups of the carrier. At 200 °C and above the carbonyl complexes decompose irreversibly with formation of oxidised forms of the metal.

In the general case the decomposition of the Group VI metal carbonyls on Al_2O_3 can be represented by the scheme[10,19]

$$M(CO)_6 + Z{-}OH \xrightarrow[-CO]{60^\circ} (Z{-}OH)M(CO)_5 \xrightarrow[-CO]{100^\circ} \rightarrow (Z{-}OH)_x M(CO)_3 \xrightarrow[-CO]{200^\circ} (Z{-}O^-)_x M^{x+} + H_2$$

This scheme includes the chemisorption of the metal carbonyls on the carrier surface, partial decarbonylation with formation of subcarbonyls at higher temperatures, and finally the complete decarbonylation and oxidation of the metal by the protons of the surface OH groups. The carriers (SiO_2, Al_2O_3) employed in the above studies were as a rule subjected to a preliminary vacuum treatment at temperatures of about 400 °C. If Al_2O_3 is subjected to a preliminary heat treatment at 950 °C, the interaction of the carbonyl with the surface proceeds differently: the decomposition of the carbonyl at temperatures above 200 °C leads to the formation of metallic molybdenum[21,23,24] or tungsten.[31] This has been explained by the appreciable decrease in the concentration of the surface OH groups in the course of the preliminary high-temperature treatment of the carrier, which stabilises the metal in the reduced state.

Table 1. The state of the metals in the thermal decomposition of chromium, molybdenum, and tungsten carbonyls on different carriers.

Initial carbonyl	Carrier	*T*, °C	State of the metal
$Cr(CO)_6$	Al_2O_3 [9,10], SiO_2 [9]	20—40	$Cr(CO)_5$ (ads.)
	Al_2O_3 [10,11], SiO_2 [12,13]	200	Cr^{2+}, Cr^{3+}
$Mo(CO)_6$	Al_2O_3 [9,14—19], SiO_2 [9]	20—40	$Mo(CO)_5$ (ads.)
	Al_2O_3 [14—16, 18—21]	100	$Mo(CO)_3$ (ads.)
	Al_2O_3 [11,14, 19—24], SiO_2 [13,14, 22,25], MgO [14], HY zeolite [26-29]	200	Mo^{3+}, Mo^{5+}
	Al_2O_3* [21,23,24], NaY [26,27]	200—500	Mo^0, Mo^{2+}
$W(CO)_6$	Al_2O_3 [9,10], SiO_2 [9,30]	20—40	$W(CO)_5$ (ads.)
	Al_2O_3 [10,31]	100	$W(CO)_3$ (ads.)
	Al_2O_3 [10,11,31], SiO_2 [12,13]	200	W^{4+}, W^{6+}
	Al_2O_3* [31]	>200	W^0

*Al_2O_3 dehyrated at 950 °C.

Analogous results have been obtained in the study of Mo-zeolitic catalysts. The decompostion of $Mo(CO)_6$ adsorbed on a type HY zeolite leads to the formation of oxidised forms of molybdenum.[26–29] On the other hand, an NaY type zeolite, containing a smaller number of OH groups, stabilises molybdenum in the zerovalent state.[26,27]

The degree of dispersion of the active component has a considerable influence on the catalytic properties of the deposited systems. Unfortunately the degree of dispersion of the metal has been determined only in a few studies. The decomposition of $Mo(CO)_6$ deposited on Al_2O_3, subjected to a preliminary heat treatment at 950 °C, leads to the formation of Mo clusters 40 Å in diameter with an overall formal charge on the metal of +0.3.[23] In contrast to metallic molybdenum, these particles do not absorb nitrogen. The authors suggest that, in the course of the decomposition of the molybdenum carbonyl on the carrier surface, Mo^{2+} ions are formed initially and then become centres for the crystallisation of zerovalent molybdenum. Such electron-deficient molybdenum clusters differ in their properties from metallic molybdenum.[23] These differences can be caused also by the different degrees of dispersion of the metal on the catalyst surface.

Thus catalytic systems containing reduced molybdenum and tungsten can be obtained by decomposing molybdenum and tungsten carbonyls on Al_2O_3 or a type NaY zeolite.

†X-Ray photoelectron spectroscopy (Ed. of Translation)].

It must be emphasised that such systems cannot be obtained from inorganic molybdenum and tungsten compounds by their reduction with hydrogen.

2. Iron Carbonyls

Numerous studies have been devoted to the interaction of complexes of iron carbonyls with the carrier surface and also to the decomposition of the surface complexes in order to obtain iron catalysts[32–57] (Table 2). The special interest in systems of this kind is due to the fact that the iron catalysts are used in industrial syntheses of hydrocarbons from CO and H_2, the synthesis of ammonia, the preparation of hydrogen, etc. IR,[32,33,35,36,38,41–43,46,47,52,54] EPR,[33,41] UV,[38,39,52] NMR,[34] and Mössbauer spectroscopy[40,41,43,55,57] and the thermoprogrammed decomposition method[39,41,42,44,50,51] are used to investigate the deposited iron carbonyl system. Since the iron carbonyl complexes are unstable in air, the systems are studied *in vacuo* or in an inert gas atmosphere.

Table 2. The state of the metal in the thermal decomposition of iron carbonyls on different carriers.

Initial carbonyl	Carrier	T, °C	State of the metal
$Fe(CO)_5$	Al_2O_3 (Refs.32, 33), MgO (Ref.32), HY zeolite (Ref.34–36), NaY zeolite (Refs.35–37)	20—40	$[HFe_3(CO)_{11}]^-$ or cluster Fe carbonyls
$Fe_2(CO)_9$	NaY zeolite (Ref.38)	20—40	»
$Fe_3(CO)_{12}$	Al_2O_3 (Refs.32, 33, 39), MgO (Refs.32, 40, 41), HY and NaY zeolites (Ref.42), SiO_2 (Ref.39), aluminosilicate (Refs. 43, 44)	20—40	»
$K_2[Fe_3(CO)_{11}]$	Al_2O_3 (Ref.45)	20—40	»
$Fe(CO)_5$	MgO* (Ref.46)	20—40	$[Fe(CO)_4]^{2-}$
$K_2[Fe(CO)_4]$	Al_2O_3 (Refs.47–49), SiO_2 (Refs.47, 48)	20—40	»
	Al_2O_3 (Refs.50, 51); MgO (Ref.46); HY and NaY zeolites (Refs.35–37, 42, 52), TiO_2 (Refs.4, 53)	40—200	$[Fe(CO)_{1-3}]_x$ (ads.)
$Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$	Al_2O_3 (Ref.54), HY zeolite (Refs.34–36, 42), TiO_2 (Ref.53), aluminosilicate (Refs.43, 44, 56)	100—300	Fe^{2+}, Fe^{3+}
	Al_2O_3 (Ref.33, 39, 47, 50, 51, 54, 55) MgO (Ref.40)	100—300	Fe^{2+}, Fe^0
	MgO* (Ref.46), NaY zeolite (Refs.35, 36, 42), graphite (Ref.37)	100—300	Fe^0

*MgO dehydrated at 800 °C.

The iron carbonyl complexes are extremely reactive. Their distinctive feature, compared with Group VI metal carbonyls, is their ability to form stable cluster structures on the carrier surface. The mechanism of the interaction of iron carbonyls with the surfaces of inorganic carriers is complex. However, it is possible to note a number of common features characteristic of these systems.

The interaction of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ with oxide carriers leads to the formation of carbonyl clusters containing three or four iron atoms on the surface.[32–44] Mononuclear complexes of the type $[Fe(CO)_4]^{2-}$ have been identified only for MgO dehydrated at 800 °C [46] and on Al_2O_3 promoted with potassium.[47–49]

It has been suggested[32,38–42] that iron carbonyls are chemisorbed on the carrier with formation of structures of types (II) and (III). As a result of this interaction, the mononuclear iron carbonyls trimerise with formation of carbonyl clusters. The stabilisation of the mononuclear complexes on MgO and Al_2O_3 is apparently caused by the appreciable decrease in the concentration of the surface OH groups as a result of the preliminary treatment or modification of the carrier.[46–49] Thus, regardless of the type of carriers and also the initial iron carbonyls, complexes having cluster structures are stabilised on the surface in most cases.

The study of the thermal decomposition of the surface carbonyl complexes *in vacuo* or in an inert gas atmosphere showed that, up to 200 °C, stable subcarbonyl species exist on the carrier surface (Table 2). The structure of these surface complexes has been studied inadequately. They are formed on decarbonylation of the initial complexes and in certain cases the process is reversible. Treatment with carbon monoxide regenerates the initial carbonyl complexes on the carrier surface.[34,37,42,43,46] Thus one of the characteristic features of the decomposition of iron carbonyls on carriers is the intermediate formation of relatively stable subcarbonyl species. The main decarbonylation product is carbon monoxide.[33,34,42,43,50,57]

Further decarbonylation at higher temperatures leads to the irreversible decomposition of the subcarbonyl species with formation of oxidised or reduced forms of iron. Together with CO, H_2 and traces of hydrocarbons are evolved under these conditions. The formation of H_2 is explained by the interaction of zerovalent iron with the protons of the surface OH groups:[34,42,50,57]

$$2Z{-}OH + Fe^0 \rightarrow (Z{-}O^-)_2Fe^{2+} + H_2 .$$

From this it follows that the ratio of the oxidised and reduced forms of iron in the deposited iron carbonyl catalyst is determined mainly by the nature of the carrier, i.e. by the properties of the surface OH groups, and also by the ratio of these groups and the active component.

The decomposition of iron carbonyls on the HY zeolite leads to the oxidation of iron to Fe^{2+}, while the NaY zeolite mainly stabilises iron in the zerovalent state.[35,36,42] Graphite has no surface OH groups and the oxidation of iron is therefore not observed on decomposition of $Fe(CO)_5$ on this carrier.[57] It has been shown that, with increase in the MgO dehydration temperature, the fraction of reduced forms of iron increases.[40,41,46] The authors explain this by the decrease in the concentration of surface OH groups during the preliminary heat treatment.

A decrease in the concentration of surface OH groups is also caused by the treatment of Al_2O_3 with potassium hydroxide.[58] It has been shown[54,55] that an increase in the fraction of the reduced forms of iron in the catalyst obtained with increase in the potassium content is observed in the decomposition of iron carbonyls deposited on Al_2O_3 subjected to a preliminary treatment with KOH.

We shall consider the available few data concerning the influence of the nature of the carrier on the degree of dispersion of the catalyst formed. Iron particles 40–50 Å in size have been obtained in the decomposition of the same iron carbonyl complex on Al_2O_3 and particles 140 Å in size have been obtained on SiO_2.[47] Particles of the active component 20–90 Å in size have been detected after the decomposition of iron carbonyls on Al_2O_3 [33] and MgO.[40] It has been established that catalysts containing more highly dispersed particles are formed on decomposition of $Fe(CO)_5$ on Al_2O_3 than in the reaction using $Fe_3(CO)_{12}$.[50,51] An increase

in the decomposition temperature of the carbonyl complexes decreases the degree of dispersion of the iron particles obtained on Al_2O_3 or graphite.[50,51,57] The synthesis of hydrocarbons from CO and H_2 on an iron carbonyl catalyst has a considerable effect on the degree of dispersion of the iron particles. After such synthesis at 270 °C at atmospheric pressure, the size of the iron particles obtained by decomposing $Fe(CO)_5$ on Al_2O_3 increased by a factor of 10–25 (to 200–500 Å).[33]

Thus the degree of dispersion of the active component in the catalyst obtained by decomosing iron carbonyls on carriers depends on a series of parameters (the conditions in the decomposition of the carbonyl complexes, the nature of these complexes, and the properties of the carrier). At the same time we may note that the carbonyl systems are characterised by a higher degree of dispersion, which is a general feature of distinguishing them from the deposited catalysts obtained from inorganic iron compounds.[53]

3. Ruthenium and Osmium Carbonyls

The ruthenium and osmium carbonyl complexes frequently manifest common properties in their interaction with the surfaces of oxide carriers and also on heat treatment[59–87] (Table 3). These systems have been investigated by the IR,[44,59–68,71–85,87] UV,[65,79] and EPR spectroscopy[86] and by the thermoprogrammed decomposition method.[44,59,64,73,77]

Table 3. The state of the metal in the thermal decomposition of ruthenium and osmium carbonyls on different carriers.

Initial carbonyl	Carrier	T, °C	State of the metal
$Ru_3(CO)_{12}$*	Al_2O_3 (Refs.59-65), SiO_2 (Refs.44, 59, 61-63, 65, 66) MgO (Ref.60), TiO_2 (Ref.61), NaY zeolite (Refs.62, 63)	25–100	$[HRu_3(CO)_{10}]$ $(OM\lessdot)$ or cluster Ru carbonyls
	Al_2O_3 (Refs.59, 61, 64, 65, 67), SiO_2 (Ref.61), TiO_2 (Ref.61)	~100	$Ru^{II}(CO)_2(OM\lessdot)_2$
	Al_2O_3 (Refs.59-64, 65, 67-72), SiO_2 (Refs.44, 59, 61-63, 65, 66), TiO_2 (Ref.61), NaY zeolite (Refs.62, 63)	>100	Ru^0, Ru (ox.)
$Os_3(CO)_{12}$**	Al_2O_3 (Refs.73-83), SiO_2 (Refs,71, 73-75, 80), MgO (Refs.84, 85), TiO_2 (Refs.73-75, 80), ZnO (Ref.75)	25–100	$[HOs_3(CO)_{10}]$ $(OM\lessdot)$ or cluster Os carbonyls
	Al_2O_3 (Refs.75-77, 81, 83, 86), SiO_2 (Refs.71, 75), MgO (Ref.85), TiO_2 (Ref.73), ZnO (Ref.75)	200–400	$Os^{II}(CO)_2(OM\lessdot)_2$
	Al_2O_3 SiO_2 (Refs.73, 74, 79, 80), TiO_2 (Refs.73, 74, 80)	200–300	Os_{12} carbonyl clusters
	Al_2O_3 (Refs.81, 87)	300	Os^0, Os (ox.)

*In Refs.59 and 60, the initial carbonyl was $H_4Ru_4(CO)_{12}$.
**In Refs.71, 73, and 74, the initial carbonyl was $Os_6(CO)_{18}$.

At temperatures up to 100 °C, the ruthenium clusters retain their structure on the surfaces of certain inorganic carriers. However, on SiO_2 and Al_2O_3 they acquire a structure of the type $[HRu_3(CO)_{10}](OM\lessdot)$.[59,61,66] A structure of type (IV) is obtained on the more basic MgO carrier.[60]

It has been shown[59] that the amount of $Ru_3(CO)_{12}$ chemisorbed on Al_2O_3 is proportional to the concentration of surface OH groups, which depends in its turn on the temperature of the preliminary treatment of the carrier.

At higher temperatures, partial decarbonylation of the surface complexes with formation of stable subcarbonyl species, apparently of the cluster type, is observed on Al_2O_3. Such species have not been detected[59] on SiO_2 but it has been established[61] that subcarbonyls are formed. The oxidation state of ruthenium in such surface complexes, formed on Al_2O_3 and SiO_2, changes from 0 to +4.[59,61,64–68] The cluster $[Ru_6C(CO)_{16}]^{2-}$ is formed on MgO.[60]

Above 100 °C, the subcarbonyl decomposes with formation of oxidised or reduced forms of ruthenium.[72] It is noteworthy that this process is reversible—treatment of the catalysts with CO at 200 °C regenerates the initial subcarbonyl, which apparently indicates a high degree of dispersion of ruthenium on the carrier surface and possibly the retention of the cluster structure of the "residues" of the complex.[59,61,69] It has been established[64,67,68] that, on decomposition *in vacuo* of the ruthenium carbonyls deposited on Al_2O_3, ruthenium produces less reduced but more highly dispersed particles than on decomposition of the above carbonyls in an H_2 atmosphere.

The degree of dispersion of ruthenium in the catalysts obtained has been determined[63,66,69,70] from the degree of adsorption of H_2 or CO. It has been shown[69,70] that the degree of dispersion of the catalyst obtained by decomposing $Ru_3(CO)_{12}$ on Al_2O_3 is four times higher than for the analogous sytems based on $RuCl_3$. Particles 20–40 Å in size have been detected on the surfaces of the latter. The size of the ruthenium crystallites obtained as a result of the decomposition of $Ru_3(CO)_{12}$ on Al_2O_3,[69] SiO_2,[66] and the NaY zeolite[63] does not exceed 10–14 Å.

The structure of the surface complexes formed as a result of the adsorption of $Os_3(CO)_{12}$ on carriers is the same as for the surface ruthenium carbonyls.[71,75–77] However, the deposited osmium carbonyls are more stable and their decomposition requires higher temperatures. At the present time there is no single view concerning the structure of osmium subcarbonyls on the Al_2O_3, SiO_2, MgO, and TiO_2 surfaces. It has been suggested[71,75–77,81,83,85] that mononuclear species of the type $Os^{II}(CO)_{2-3}$(ads.) are stabilised on the carrier surface. On the other hand, it has been concluded[73,74,79,80,84] that the subcarbonyls formed have a cluster structure and that they incorporate up to 12 osmium atoms. Such differences have been explained[73] by the different preliminary types of treatment of the carrier. It has been suggested that osmium carbonyl clusters are stabilised on carriers dehydrated to a high degree and that a high concentration of surface OH groups leads to the dissociation of the Os–Os bonds and the formation of mononuclear species. Further studies are necessary in order to establish reliably the structure of the subcarbonyl species and also the factors which determine the latter.

Osmium subcarbonyls on the Al_2O_3, SiO_2, TiO_2, and MgO surfaces are distinguished by a high stability and do not decompose *in vacuo*, in an inert gas atmosphere, or in an atmosphere consisting of a mixture of CO and H_2 even at 300–400 °C.[75,76,84–86] However, the formation of metallic osmium has been observed after the treatment of the catalyst in an H_2 atmosphere at 300 °C.[81]

It has been suggested[75,84–87] that the degree of dispersion of osmium in the catalysts investigated is very high and that its distribution is close to being molecular.

Having compared the ways in which iron, ruthenium, and osmium carbonyls interact with the surfaces of inorganic carriers, one may conclude that the formation of surface carbonyl complexes with a cluster structure is characteristic of all these systems. Their thermal stability increases in the sequence Fe < Ru < Os. In certain cases,[75,82,84] surface

osmium carbonyls are detected in the catalyst after the synthesis from CO and H_2 at atmospheric pressure and temperatures in the range 300–400 °C.

4. The Carbonyls of Other Group VIII Metals

The interaction of cobalt, rhodium, and iridium carbonyls with inorganic carriers has been little studied. It has been demonstrated by IR spectroscopy that tetranuclear cluster carbonyls are formed on the Al_2O_3, SiO_2,[88–92] MgO, TiO_2, and ZrO_2 [90] surfaces, The structures of these complexes apparently correspond to structure (III). On the other hand, it has been found that[93] $Co_3(CO)_9CH_3$ disproportionates on the surfaces of Al_2O_3, SiO_2, or the NaY zeolite with formation of Co^{2+} and $[Co(CO)_4]^-$ and that the carriers can be arranged in the following sequence in terms of the rate of this reaction: Al_2O_3 > NaY > SiO_2.

The study of the thermoprogrammed decomposition of cobalt carbonyl complexes on Al_2O_3 and SiO_2 showed[88,89,91] that, up to 100–150 °C, the relatively stable subcarbonyl complexes exist on the surface. At higher temperatures these species decompose irreversibly with formation of metallic cobalt and its oxidised forms.[89–92,94,95]

The degree of dispersion of the active component on the carrier surface depends on the conditions in the preparation of the catalyst and also on the nature of the carrier. An increase in the rates of temperature rise during the decomposition of surface carbonyl complexes leads to the formation of more dispersed catalysts.[92,94] The cobalt particles size on SiO_2 is greater than on Al_2O_3 and TiO_2. In certain cases it is possible to obtain systems containing cobalt crystallites 20–50 Å in size.[92] The lower degree of dispersion of the Co/SiO_2 catalysts has been explained[92] by the weak bond between the carbonyl complexes and the surface. Modification of the SiO_2 surface by titanium hydride complexes promotes the growth of the degree of dispersion of the metal in the cobalt catalysts.[96]

As in the case of cobalt carbonyls, the interaction of rhodium carbonyls with the SiO_2 surface does not alter the structure of the initial complexes.[97–99] On the other hand, the adsorption of $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, or $[Rh(CO)_2Cl]_2$ on Al_2O_3 from the gas phase or an organic solvent followed by treatment with CO leads to the formation of only the one complex $Rh_6(CO)_{16}$ on the surface.[97,99,100] In the interaction of $Rh_6(CO)_{16}$ with Al_2O_3 or MgO, the surface mononuclear carbonyl $Rh^I(CO)_2$ (OM–) (here M = Al or Mg) was identified by IR spectroscopy.[101,102]

At 100–200 °C *in vacuo* or in an H_2 atmosphere, the surface rhodium carbonyls decompose with formation of metal crystallites[100,103,104] whose size is close to 10 Å.[103] In the course of the decomposition of rhodium carbonyls on carriers, the intermediate formation of subcarbonyl surface complexes was discovered.[95,98,102,104,105] In contrast to pure H_2, in the presence of a mixture of CO and H_2, the surface carbonyl complexes are present together with metallic rhodium on the ZnO surface even at 400 °C.[104]

The interaction of $Ir_4(CO)_{12}$ with Al_2O_3 and SiO_2 has been investigated[106,107] by IR spectroscopy. At 20–100 °C the carbonyl is physically adsorbed on the carrier surface, to a lesser extent on SiO_2 than on Al_2O_3. Iridium carbonyl decomposes on carriers *in vacuo* at 100–200 °C with the intermediate formation of subcarbonyl mononuclear species of the type of $Ir(CO)_2$(ads.).[107] On raising the temperature to 300 °C, the surface iridium complexes are converted irreversibly into metallic iridium. Oxidised forms of iridium are then also formed on Al_2O_3 under these conditions and are reduced to the metal on treatment with H_2 at 300 °C.[108,109] According to Anderson and Howe,[108] the size of the iridium crystallites is approximately 10 Å, while Tanaka et al.[109] state that species incorporating about 20 iridium atoms are formed.

It has been established by IR spectroscopy that a complex of the type $Ni(CO)_nL_{4-n}$ (n = 2, 3; L = Ph_3P or Al_2O_3) is formed at room temperature as a result of the adsorption of $Ni(CO)_4$ on Al_2O_3 containing Ph_3P.[110] The decomposition of $Ni(CO)_4$ adsorbed on Al_2O_3, HY and NaY zeolites,[111] and NaX and CaX zeolites,[112,113] has been investigated. The size of the metallic nickel crystallites is 500–2000 Å on Al_2O_3 [111] and less than 30 Å on type X zeolites.[113] The decomposition of the carbonyl on zeolites proceeds with the intermediate formation of subcarbonyl complexes with the ratio Ni : CO = 1. It has been suggested[113] that the nickel crystallites are localised within the zeolite cavities and that this prevents the aggregation of the highly dispersed particles.

Highly dispersed platinum catalysts with metallic platinum particle size less than 10 Å have been obtained by decomposing the complexes $[NEt_4][Pt_3(CO)_6]_n$ (n = 1–5) deposited on SiO_2 or Al_2O_3.[114] The carbonyl complexes were decomposed at 160–250 °C *in vacuo* or in an H_2 atmosphere.

The interactions of heterometallic carbonyl clusters with inorganic carriers have been studied in a number of investigations[115–124] in order to obtain highly dispersed bimetallic particles on their surfaces. It has been shown[115] that the interaction of the $H_2RuOs_3(CO)_{13}$ cluster with Al_2O_3 in an atmosphere of CO and H_2 at 100–200 °C results in the formation of the $[H_3RuOs_3(CO)_{12}]^-$ anion on this surface. On the other hand, $H_3FeOs_3(CO)_{13}$ on SiO_2 decomposes at 130 °C in argon, forming metallic iron and $HOs_3(CO)_{10}(O–Si\leq)$.[116] The osmium cluster formed is fully decarbonylated at temperatures above 250 °C with formation of metallic osmium, whose particle size is about 16 Å.[116]

It has been suggested that the decomposition of $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ on ZnO [105,117] and $Co_2Rh_2(CO)_{12}$ on SiO_2 [118] leads to the formation of highly dispersed bimetallic particles. It has been shown[119] that the decomposition of $Co_2Rh_2(CO)_{12}$ or $Co_3Rh(CO)_{12}$ on Al_2O_3 at 400 °C in hydrogen makes it possible to obtain bimetallic clusters in which the ratio of the metals remains approximately the same as in the initial carbonyl complexes. Catalysts of analogous composition, obtained by the deposition of the salts $RhCl_3$ and $CoCl_2$, are much less dispersed.[119]

Bimetallic catalysts containing particles 15–30 Å in size have been obtained from $H_2RhOs(CO)_{10}$(acac) and $H_2FeOs_3(CO)_{12}$ using Al_2O_3 as the carrier.[120]

The decomposition of the carbonyls $Fe_nRu_{3-n}(CO)_{12}$ (n = 1–3) on charcoal leads to the formation of Fe–Ru crystallites whose surface is enriched in iron.[121] The use, instead of the bimetallic cluster, of a mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ having the same composition altered appreciably the properties of the catalysts.

A similar study of the properties of catalysts obtained by decomposing $Ru_3(CO)_{12}$ on a reduced Pd/SiO_2 catalyst[122–124] showed that at room temperature the carbonyl is adsorbed on the surface and is then partly oxidised. The subsequent reduction of the catalyst with hydrogen leads to the formation of bimetallic Ru–Pd particles whose size is less than 16 Å.

Thus, catalysts containing the reduced metals can be obtained by decomposing transition metal carbonyls on inorganic carriers. It is noteworthy that the decomposition conditions and also the nature of the carbonyl and the carrier influence significantly this process. During the decomposition of almost all metal carbonyls, the formation of intermediates subcarbonyl complexes on the carrier surfaces was observed. At the present time the influence of various factors on the degree of dispersion of the active component in the catalyst obtained has not as yet been adequately elucidated. Nevertheless, there is no doubt that the catalysts

obtained from metal carbonyls are characterised by a higher degree of dispersion than those prepared from inorganic compounds. This is apparently caused by the mild preliminary treatment of the metal carbonyl catalyst. We may note that the metal-deposited systems, prepared by traditional methods, are usually reduced with hydrogen at high temperatures, which leads to the sintering of the metal into large crystallites.

III. SYNTHESIS OF ORGANIC COMPOUNDS FROM CO AND H_2 IN THE PRESENCE OF METAL CARBONYL CATALYSTS

As stated above, deposited metallic catalysts, obtained from metal carbonyls, are distinguished from traditional systems having the same composition by a higher degree of dispersion and a higher degree of reduction of the active component. In particular, metal carbonyl catalysts are therefore characterised by a higher specific activity in the synthesis of hydrocarbons or oxygen-containing compounds from CO and H_2.

The use of polymetallic carbonyl clusters makes it possible to obtain in a number of instances catalysts with unique properties, frequently exhibiting a high selectivity in many chemical reactions.

1. Molybdenum and Tungsten Catalysts

Molybdenum and tungsten carbonyl catalysts, deposited on Al_2O_3 and containing from 1% [20,23,24] to 3–5% [125,126] of molybdenum or tungsten, are used for syntheses from CO and H_2. The activity of the molybdenum catalysts is approximately 5 times greater.[23,24] Comparison of the molybdenum and tungsten carbonyl catalysts with traditional systems of analogous composition has shown that the latter are less active. This has been attributed to the higher degrees of reduction and the greater degree of dispersion of the active component in the carbonyl systems.[23,24,125,126] Preliminary treatment of the carrier before the adsorption of the carbonyl has an appreciable influence on the activity of the molybdenum carbonyl catalyst. In a flow system at atmospheric pressure at 300 °C, the activity of the catalysts based on Al_2O_3 heat-treated at 950 °C is 0.04 mol CH_4 (g-atom Mo)$^{-1}$ s^{-1}, while that for Al_2O_3 heated at 500 °C is 0.001 mol CH_3 (g-atom Mo)$^{-1}$ s^{-1},[23,24] which is apparently due to the lower degree of reduction of molybdenum in the latter case.

The principal products of the synthesis from CO and H_2 in the presence of molybdenum carbonyl complexes at atmospheric pressure are CH_4 and CO_2. Together with the latter, C_2H_6 and C_3H_8 are formed in much smaller amounts.[23,24] A mixture of C_1–C_6 hydrocarbons, with CH_4 and C_2H_6 predominating, has been obtained from CO and H_2 at 25 atm, 350 °C, and a volume flow rate of 1300 h^{-1}.[125] Promotion of the molybdenum carbonyl catalyst with 4% of potassium lowers the activity and increases the fraction of olefins in the synthesis product, whose content does not, however, exceed several per cent.[125] The activity and selectivity of the catalyst remained unchanged during 5–20 h of their use.[23,24,125] A mixture of C_1–C_4 hydrocarbons, with the contents of CH_4 (60%) and C_2H_6 (25%) predominating, has been obtained from CO and H_2 at 350 °C and 25 atm in the presence of a tungsten carbonyl complex based on Al_2O_3.[126]

2. Iron Catalysts

The considerable interest shown by investigators in iron carbonyl catalysts is due to the high selectivity of these systems in the synthesis of light olefins from CO and H_2 and also by the ready availability and low cost of $Fe(CO)_5$. Unfortunately, comparison of the results obtained by different authors is not always possible because different methods are used even for synthesis of catalysts having the same composition. This also applies to the methods of synthesis from CO and H_2.

Iron carbonyl catalysts based on Al_2O_3, SiO_2, MgO, La_2O_3, and MnO exhibit a high selectivity in the synthesis of light olefins from CO and H_2, whose yield can exceed 50% at 170 to 300 °C and 1–10 atm.[33,40,127–129] The greatest fraction is that of C_3H_6, which falls somewhat under the conditions where the catalyst has been used for a long time.[33] At the same time a decrease of the degree of dispersion of the catalyst is observed. On these grounds, the authors[33] concluded that light olefins are synthesised from CO and H_2 on highly dispersed particles of the active component of the catalyst.

At 250 °C, the highest activity is shown by catalysts based on MgO, while those incorporating Al_2O_3, SiO_2, TiO_2, and ZrO_2 are less effective.[130] The composition of the synthesis products in the presence of all these systems is approximately the same. Thus the CH_4 content is 27–37%, while the proportion of olefins in the C_2–C_3 fraction is 72–96%.[130]

The physicochemical and catalytic properties of systems obtained by decomposing potassium carbonyl ferrates on Al_2O_3 and SiO_2 have been studied in detail.[47] A mixture of C_1 and C_6 hydrocarbons, whose olefin content exceeds 50%, is formed in the presence of these systems from CO and H_2 at 270 °C and atmospheric pressure. The degree of conversion of CO was 2–7% on the Al_2O_3-based catalyst and 0.2% on the SiO_2-based catalyst. Catalysts of analogous composition, prepared using inorganic compounds (salts) of iron and potassium, show an activity smaller by a factor of 40–50.[47] The change in the atomic ratio K : Fe in the carbonyl catalysts from 2 to 1 for an overall iron content of 3% tends to increase the activity by a factor greater than 3 with the simultaneous diminution of the yield of olefins and C_5–C_6 hydrocarbons and an appreciable decrease in the activation energies for the methane formation and conversion reactions of CO.[47]

The influence of the conditions of the synthesis from CO and H_2 and also of the composition of the Fe/Al_2O_3 carbonyl catalysts promoted with potassium on its activity and selectivity has been investigated.[45,49,55,131,132] Comparison of the catalysts obtained from $Fe(CO)_5$ [49,132] and $Fe_3(CO)_{12}$ [45,131] showed that, for the same iron and promoting agent contents, they exhibit identical properties in synthesis from CO and H_2. The main products of the synthesis in the presence of these systems at 350–450 °C were CH_4, C_2H_4, C_3H_6, and CO_2. The increase in the iron content in the catalyst from 0.15 to 1.8% for a constant content of the promoting agent (potassium) lowered the fraction of ethylene and propene in the products of the synthesis from 70 to 40% and increased the degree of conversion of CO from 4 to 20%.[132] The Fe–K–Al_2O_3 catalysts containing 7–8% of potassium exhibit the highest activity.[131,132] The increase in the activity of the Fe–K–carbonyl catalyst with increasing content of potassium in the latter has been attributed[55] to the decrease in the fraction of the oxidised form of iron formed on decomposition of the initial carbonyl complexes. The increase in the selectivity of the Fe–K–Al_2O_3 catalyst in the formation of ethylene and propene is favoured by a decrease in the temperature of the synthesis (from 450° to 350 °C), by a decrease in the H_2 : CO ratio (from 4 : 1 to 1 : 3), and also by an increase in the volume flow rate of CO and H_2 (from 15 to 100 h^{-1}).[131]

Type Y zeolites can be used as carriers for iron carbonyl catalysts,[37,42,133] The main products of the synthesis from CO and H_2 under static conditions in the presence of iron catalysts containing the HY, NaY, and CaY zeolites at 1–20 atm and 250–400 °C were C_1–C_4 alkanes and also CO_2.[37,42]

The increase in the iron content from 3 to 8% led to an appreciable growth of the activity of these systems.[37] Mixtures of C_1–C_4 hydrocarbons containing up to 30% of ethylene and propene have been obtained in a flow system in the presence of iron carbonyl catalysts containing the BeY, MgY, CaY, SrY, and BaY zeolites at 1 atm and temperatures in the range 300–400 °C.[133] In terms of their activity in the synthesis of hydrocarbons from CO and H_2, the above catalyst can be arranged in the sequence BaY > SrY > CaY > MgY > BeY. It is the same as the sequence based on the increase in the acid properties of the carriers—type Y zeolites.[133]

Iron carbonyl catalysts of the synthesis of hydrocarbons from CO and H_2 can undoubtedly be of practical value. Analysis of patent literature[48,134–137] shows that effective catalytic systems, based on deposited iron carbonyls and permitting the synthesis of lower olefins from CO and H_2 with a high selectivity, have now been created.

3. Ruthenium and Osmium Catalysts

The properties of ruthenium and osmium carbonyl catalysts in syntheses from CO and H_2 depend greatly on the experimental conditions. As stated above, at temperatures up to 200 °C, these systems are reversibly decarbonylated. Thus, when the synthesis is carried out in the above temperature range, the catalyst surface contains, together with the oxidised and reduced forms of the active component, also cluster carbonyl complexes, which has a definite influence on the activity and selectivity of the above systems.

It has been shown[33,47,48,60] that at 200 °C and 1–20 atm the activity of the ruthenium carbonyl catalyst containing Al_2O_3 is higher than that of traditional systems. At the same time the composition of the hydrocarbons obtained (C_1–C_5) differs insignificantly from that of the product of synthesis in the presence of catalysts prepared from inorganic ruthenium compounds. When ruthenium carbonyls are deposited on MgO, the ruthenium carbonyl cluster persists on the catalyst surface during the synthesis from CO and H_2 and it has been possible to isolate it after the synthesis and to identify as $[Ru_6C(CO)_{16}]^{2-}$.[60] A distinctive feature of such systems is their lower activity and also the high content of olefins in the hydrocarbon mixtures formed (23–28%). At the same time up to 21–27% of C_1–C_2 alcohols are formed.[60] A mixture of C_1–C_6 hydrocarbons containing up to 80% of olefins has been obtained from CO and H_2 at 200 °C and 500 mmHg in the presence of the $Ru_3(CO)_{12}/Al_2O_3$ catalyst.[70] Promotion of the ruthenium carbonyl catalyst with potassium lowers its activity and increases its selectivity in relation to the formation of olefins. The introduction of boron or phosphorus into the catalyst produces the opposite results.[138] The $Ru_3(CO)_{12}/CeO_2$ catalyst, in the presence of which a mixture of hydrocarbons containing 35% of C_2–C_4 olefins was obtained from CO and H_2, has been proposed.[139]

Catalysts active in the synthesis of C_1–C_5 hydrocarbons at 270 °C have been obtained using $Na[HRu_3(CO)_{11}]$. In terms of their activity, these catalysts on different carriers can be arranged in the following sequence of the latter Al_2O_3 > SiO_2 > MgO > TiO_2. Catalysts containing TiO_2 and MgO are the most selective in the formation of ethylene and propene.[140]

At temperatures of about 300 °C and above, methane is formed as the main product from CO and H_2 in the pesence of ruthenium carbonyl catalysts containing SiO_2,[128,141] Al_2O_3, or the NaY zeolite.[141] Methane is also produced selectively from mixtures of CO_2 and H_2 in the presence of the above ruthenium carbonyl systems.

Catalysts obtained by adsorbing $Ru_3(CO)_{12}$ on type NaX, NaY, KL, and NaM zeolites and also SiO_2 have been investigated.[142,143] The metal content in the catalyst was from 0.4 to 1.4%. In terms of their specific activity, the catalysts on different carriers can be arranged in the sequence NaY > NaX > NaM > KL, SiO_2.[142] The activation energy for the conversion of CO in the presence of these catalysts is about 23 kcal mol^{-1}. At 250 °C and 1 atm, the main products of the synthesis were C_1–C_5 hydrocarbons. The $Ru_3(CO)_{12}$/NaY catalysts proved to be the most selective as regards the formation of olefins and made it possible to obtain up to 45% of C_2–C_4 olefins under the conditions indicated. The increase in the temperature of the synthesis from 200° to 340 °C increases the fraction of methane and reduces the olefin/paraffin ratio in the synthesis products.[142] A ruthenium carbonyl catalyst on the HM zeolite has been proposed for the synthesis of C_1–C_7 hydrocarbons, including up to 69% of C_4–C_5 hydrocarbons, from CO and H_2.[144]

There have been only a few studies of the catalytic properties of osmium carbonyl catalysts.[33,80–82,84,87] In particular, the kinetics of the conversion of CO and CO_2 into methane at 180–400 °C has been studied.[80] In terms of their activity these catalysts can be arranged in the sequence SiO_2 > TiO_2 > Al_2O_3 as a function of the carriers used.[80] A mixture of C_1–C_4 hydrocarbons has been obtained in the presence of osmium catalysts based on SiO_2 at 200 °C [33] or on MgO at 300 °C.[84] As for the ruthenium systems, the osmium carbonyl catalysts containing the active component in the metallic state are more active than the catalysts on the surfaces of which the carbonyl complexes are present.[81,82] The introduction of potassium into the osmium carbonyl catalysts[82] increases their selectivity in relation to the formation of olefins.

It has been shown[87] that osmium catalysts based on Al_2O_3 are active in the synthesis of C_1–C_7 alkanes at 250–300 °C and 10 atm. Their activity increases with decrease in the degree of dispersion of the metallic osmium. It has been suggested[87] that the active centres for the synthesis of alkanes are metallic osmium clusters and those for the synthesis of oxygen-containing compounds are carbonyl complexes on the catalyst surface.

4. Cobalt Catalysts

In the presence of cobalt carbonyl catalysts, the main products of the synthesis from CO and H_2 are saturated hydrocarbons with a normal structure. It has been shown[145–147] that the pore diameter in the carrier (Al_2O_3, aluminosilicate) influences decisively the process selectivity: a decreases in the pore diameter shifts the selectivity maximum towards the formation of lighter hydrocarbons without altering the catalyst activity. For example, the main products of the synthesis in the presence of the 2% CO/Al_2O_3 catalyst at 200 °C and with an average carrier pore diameter of 300 nm are C_{14}–C_{20} alkanes, while for an average pore diameter of 6.5 nm the main products are C_4–C_9 alkanes.[147] The authors[147] explain this phenomenon by selective condensation (as a function of the molecular weight) within the catalyst pores of the hydrocarbons formed during the synthesis with their subsequent hydrogenolysis to lighter hydrocarbons. However, these features are valid only for systems in which almost the entire cobalt is present in the catalyst pores, i.e. for catalysts containing small amounts of cobalt (several per cent).

The influence of the nature of the carrier and also of the conditions in the preparation of the cobalt carbonyl catalyst (1–4% CO) on its properties in the synthesis of hydrocarbons for CO and H_2 has been studied in detail.[90–92,94,148–152] It has been shown that,[92,94] when the temperature is raised rapidly in the decomposition of carbonyl complexes, the latter break down with formation of highly dispersed metallic particles on the SiO_2, Al_2O_3, and TiO_2 surfaces. These

catalysts exhibit an activity exceeding by a factor of 2–10 the activity of systems based on inorganic cobalt compounds. If the decomposition is carried out with a slow temperature rise (~1 K min^{-1}), less dispersed catalysts are formed and exhibit a low activity in the synthesis of organic compounds from CO and H_2. The main products of the synthesis using cobalt catalysts on Al_2O_3, MgO, SiO_2, TiO_2, and ZrO_2 containing 1–24% CO are, at 160–180 °C, C_4–C_{22} hydrocarbons with the normal structure.[148] It has been suggested that[148] in this instance α-olefins are intermediates in the synthesis of the alkanes. In terms of their activity the above catalysts can be arranged in the following sequence based on the nature of the carrier: $SiO_2 > TiO_2 > ZrO_2 \geq Al_2O_3 > MgO$.[92]

Cobalt catalysts on TiO_2 and ZrO_2 manifest a high selectivity in relation to the formation of higher molecular weight hydrocarbon fractions.[92,149] An increase in the surface concentration of cobalt and also preliminary partial oxidation of the catalyst with air shift the selectivity maximum towards the formation of heavier hydrocarbons.[149] It is noteworthy that, in the presence of the Co/MgO and Co/Al_2O_3 catalysts, up to 25% of alcohols is formed together with hydrocarbons.[148] It has been concluded[96] that an increase in the degree of dispersion of cobalt lowers the specific activity of the catalyst and increases the fraction of light hydrocarbons as well as oxygen-containing compounds in the synthesis products.

The synthesis of hydrocarbons from CO and H_2 in the presence of cobalt carbonyl catalysts (5–15% Co) has been investigated.[91,150,152] The main products of the synthesis at 180–200 °C and atmospheric pressure were C_5–C_{22} hydrocarbons. The properties of the catalyst were estimated from the yields of the liquid hydrocarbons (B_L) per nm^3 of the mixture with the volume ratio $CO:H_2 = 1:2$ at a volume flow rate of 100 h^{-1}. In the absence of promoting agents, $B_L = 42$ nm^{-3} for the catalyst with 5–7% Co on Al_2O_3 and 28–34 g nm^{-3} for the catalyst with the same metal content on SiO_2.[150–152] Promotion of Co/SiO_2 by metal oxides (MgO, NiO, ZrO_2, and CoO) increases B_L.[151] Thus the introduction of up to 30% of CoO into the 7% Co/SiO_2 catalyst induces a sharp increase in B_L to 83 g nm^{-3}.[151,152] When a high-silica zeolite of the pentasil type is used as the carrier ($SiO_2:Al_2O_3 = 42$), the yields of liquid hydrocarbons are low, but the composition of the synthesis product differs appreciably from that obtained in the presence of the Co/Al_2O_3 or Co/SiO_2 catalysts.[152] The paraffins formed in the presence of the Co-zeolitic catalyst consisted mainly of C_5–C_{14} hydrocarbons and their content of isoalkanes reached 44%. A characteristic feature of these catalysts is also the presence in the synthesis products of small amounts of aromatic hydrocarbons.[152] The properties of cobalt carbonyl catalysts on SiO_2 and Al_2O_3 are appreciably influenced by the conditions in their preliminary treatment and by the gas employed in this process (CO, CO + H_2, Ar). Preliminary treatment of the catalyst with a mixture of CO and H_2 at 150 °C proved to be optimal.[91]

The kinetics of the synthesis of C_1–C_5 hydrocarbons from CO and H_2 in the presence of cobalt carbonyl catalysts (1.2–1.9% Co) has been investigated.[153] At 220 °C and for the ratio $CO:H_2 = 1:3$, the rates of reaction were 2.5×10^{-4} mol CO (g-atom Co)$^{-1}$ s^{-1} in the presence of Co/Al_2O_3 and Co/ZrO_2 and 4.4×10^{-4} mol CO (g-atom Co)$^{-1}$ s^{-1} in the presence of Co/SiO_2.

The activity of the cobalt carbonyl catalyst depends on the structure of the initial cobalt cluster. The catalyst obtained by depositing $Ph_2C_2Co_4(CO)_{12}$ on Al_2O_3 is the most active.[154] It has been established that the catalyst obtained by decomposing $Co_2(CO)_8$ or $Co_4(CO)_{12}$ on SiO_2 fully converts the $CO:H_2 = 1:2$ mixture into methane and CO_2 at 300–450 °C and a volume flow rate of 500 h^{-1}. A highly active cobalt catalyst promoted with palladium or platinum has been proposed for the synthsis of hydrocarbons.[155]

5. Rhodium, Iridium, and Platinum Catalysts

A distinctive feature of deposited rhodium, iridium, and platinum carbonyl catalyst is their high selectivity in relation to the formation of methanol and ethanol from CO and H_2. The catalyst obtained from $Rh_4(CO)_{12}$ and ZnO, CaO, or MgO showed the greatest selectivity in relation to the formation of methanol (91–99%) at 200–220 °C and 1 atm.[156–158] Using TiO_2, ZrO_2, ThO_2, amd CeO_2 as carriers for the rhodium carbonyl catalyst, it is possible to direct the process selectivity towards the predominant formation of ethanol from CO and H_2. Rhodium systems on SiO_2 and Al_2O_3 catalyse the formation of C_1–C_4 hydrocarbons.[33,156–158] It has been suggested[156] that, with decrease in the basicity of the carrier and with increase in its acidity, the selectivity of the catalyst in relation to the formation of oxygen-containing compounds diminishes and that in relation to the formation of hydrocarbons increases. The kinetics of the synthesis of CH_4 and ethanol in the presence of rhodium catalysts has been studied.[153] At 220 °C and for the ratio $CO:H_2 = 1:3$, the rates of reaction were 1.2×10^{-4} (Rh/Al_2O_3), 2.2×10^{-3} (Rh/ZrO_2), and 4×10^{-5} mol CO (g-atom Rh)$^{-1}$ s^{-1} (Rh/SiO_2). For the catalyst on ZrO_2, the rate of formation of methane under these conditions is 10 times greater than the rate of synthesis of ethanol. In the presence of catalytic systems on Al_2O_3 or SiO_2, mainly only hydrocarbons were formed from CO and H_2.[153]

The structure of the initial rhodium carbonyl cluster exerts a significant influence on the course of the synthesis in the presence of rhodium catalysts on La_2O_3.[156,158] Catalysts synthesised from $Rh_4(CO)_{12}$ and $Rh_6(CO)_{12}$ are the most active and selective in relation to the formation of alcohols. A method of synthesis of ethanol from CO and H_2 at 250 °C and 25 atm in the presence of the $Rh_6(CO)_{16}/ThO_2$ catalyst promoted with 1% Eu has been proposed.[159]

Iridium carbonyl catalysts on Al_2O_3 catalyse the formation of C_1–C_4 alkanes at 180–285 °C and 1 atm, the main product being CH_4 (72–78%).[33,47] On the other hand, the formation of methanol as well as methane was observed in the presence of the $Ir_4(CO)_{12}/ZnO$ catalyst.[157]

Catalysts based on cluster platinum carbonyls and ZnO or MgO are characterised by a high selectivity in relation to the formation of methanol (94–99%) at 170–260 °C and atmospheric pressure.[157]

6. Catalysts Based on Bimetallic Carbonyl Clusters

A promising trend in the synthesis of heterogeneous catalysts involves the use of bimetallic transition metal carbonyl clusters in the preparation of new catalytic systems. Polymetallic carbonyl clusters of almost all the Group VIII elements have now been synthesised.[160] The study of catalysts obtained by the thermal decomposition of bimetallic carbonyl clusters on the surfaces of inorganic carriers was initiated several years ago, but results demonstrating the promising nature of this procedure have already been obtained.

Catalysts obtained by decomposing the $H_2FeRu_3(CO)_{13}$ and $Fe_2Ru(CO)_{12}$ clusters and a mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ on SiO_2 have been tested in synthesis from CO and and H_2 at 250–280 °C and 1–19 atm.[128,161] The catalyst based on $H_2FeRu_3(CO)$, in the presence of which methane is mainly formed from CO and H_2, showed the highest activity. The catalyst based on $Fe_2Ru(CO)_{12}$ was less active but more

selective in relation to the formation of olefins. It is noteworthy that, when the Ru–Fe cluster was replaced by the equivalent mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$, the activity and selectivity of the specimen did not change. On the other hand, the opposite result has been described:[121] the replacement of catalysts obtained by decomposing $Fe_nRu_{3-n}.(CO)_{12}$ ($n = 0-2$) on charcoal by catalyst prepared from the mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ altered the catalytic properties of the system. The main products of the synthesis in the presence of these systems at 275 °C were C_1-C_4 alkanes.

Effective catalysts for the conversion of CO into methane have been obtained by decomposing the complex $H_2FeRu_3.(CO)_{13}$ on Al_2O_3, SiO_2, or the NaY zeolite.[141]

It has been shown[116] that, in terms of its activity and selectivity in the synthesis of C_1-C_4 hydrocarbons at 250 °C and 1 atm, the $H_2FeOs_3(CO)_{13}/SiO_2$ catalyst occupies an intermediate place between the $Fe_3(CO)_{12}/SiO_2$ and $Os_3(CO)_{12}/SiO_2$ catalysts.

The synthesis from CO and H_2 in the presence of the $H_2FeOs_3(CO)_{13}/Al_2O_3$ catalyst at 270 °C and 10 atm yielded CH_4 (49%), C_2H_6(11%), and $(CH_3)_2O$ (36%).[120] The $H_3CpNi.Os_3(CO)_9/Al_2O_3$ catalyst, active in the synthesis of CH_4 and C_2H_6 from CO and H_2 at 250–350 °C, has been described.[162]

The properties of the catalysts obtained by decomposing the cluster anion $[FeCO_3(CO)_{12}]^-$ depend greatly on the nature of the carrier. When aminated silica gel was used as the carrier,[163] a catalyst for the selective synthesis of light olefins from CO and H_2 at 240 °C and 1–40 atm was obtained. A characteristic feature of this catalytic system is the reduced content of olefins and the shift of the selectivity maximum towards light hydrocarbons with increase in pressure. On the other hand, the decomposition of $[FeCo_3(CO)_{12}]^-$ on SiO_2 promoted with titanium hydride complexes makes it possible to obtain a system which catalyses the formation of methanol (10%) and ethanol (30%) together with hydrocarbons at 180 °C and 1 atm.[164]

The introduction of platinum into the iron carbonyl catalyst greatly increases the activity with retention of a high selectivity in relation to the formation of light olefins.[165] The authors[165] suggest that, under the conditions of the preparation of the catalyst and the synthesis from CO and H_2, the platinum surface is partly coated by iron, which is responsible for the increase in activity.

The properties of catalysts based on $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_4(CO)_{12}$, and $Rh_4(CO)_{12}$ on Al_2O_3, SiO_2, and ZrO_2 have been investigated.[153] At 200–220 °C and for the ratio $CO:H_2 = 1:3$, the main products of the synthesis were methane and ethanol. The bimetallic Co–Rh catalyst occupies an intermediate position between the cobalt and rhodium catalysts as regards activity. An increase in the Co:Rh ratio lowers the rate of conversion into methane and to a lesser extent, the rate of synthesis of ethanol. The maximum selectivity in relation to the formation of ethanol is reached for the ratio $Co:Rh = 1:1$.[153]

A comparative study of catalysts based on $Fe_3(CO)_{12}$ and $[NEt_4]_2[Fe_2Mn(CO)_{12}]$ on various carriers (Al_2O_3, SiO_2, MgO, TiO_2, and ZrO_2) has been carried out.[130] With the exception of the catalyst incorporating MgO, they all yield comparatively little methane and a large amount of heavy hydrocarbons in the synthesis. It is noteworthy that in this respect they differ from the catalysts of analogous composition obtained from iron and manganese nitrates. The authors[130] suggest that the Fe–Mn interaction takes place on the carrier surface also after the decomposition of the metallic cluster, in contrast to systems obtained by the decomposition of nitrates.

The Pd–Ru crystallites have been obtained[124] on the SiO_2 surface by adsorbing $Ru_3(CO)_{12}$ on the Pd/SiO_2 catalysts and by subsequent treatment with hydrogen. An increase in the Pd/Ru ratio drives the synthesis from CO and H_2 towards the preferential formation of methanol and the activity of the catalyst then passes through a minimum.

Thus the use of polymetallic carbonyl clusters for the preparation of catalysts constitutes a promising method of synthesis of highly dispersed catalysts. The fact that the additivity of the properties of the catalysts obtained by the separate deposition of the complexes is not observed in many instances, which indicates the possibility of the interaction of transition metals also after the decomposition of the carbonyl clusters, merits special attention.

IV. CONCLUSION

The synthesis of organic compounds from CO and H_2 is a complex and in most cases a multistage process incorporating consecutive and parallel reactions, the key stages of which are those involving the growth and termination of the hydrocarbon chain and also hydrogenation. The composition of the products of synthesis is influenced very strongly, together with the type of the catalyst employed, by the reaction conditions (temperature, pressure, volume flow rate, the ratio of CO and H_2, etc.). Therefore, as a consequence of the difference between the conditions and methods of synthesis, comparison of the results obtained in different studies in the presence of carbonyl catalytic systems having identical or similar compositions is not always possible.

This comparison is also hindered by two other factors. Different workers have used different carriers for the deposition of metal carbonyls and also different methods of deposition of the carbonyls and of the preliminary treatment of the catalyst. Furthermore, the methods employed to test the catalysts also differed: the contact time was varied from 1–2 h at a constant temperature to 5–20 days with a temperature rise. By analysing the above data, one can therefore achieve only the most general conclusions and comparisions.

Mainly metal carbonyl catalysts based on Group VI and VIII metals are active in the synthesis of light hydrocarbons and, in particular, of methane. In this case, the chain termination stage apparently predominates over the propagation stage. For example, the preferential formation of methane from CO and H_2 has been described for deposited molybdenum and tungsten,[20,23,24,125,126] iron,[37] ruthenium,[128,141] osmium,[33,80] cobalt,[141] rhodium,[153] and iridium catalysts.[33,47,157] The synthesis of C_1-C_4 hydrocarbons in the presence of iron,[37,42] ruthenium,[33,47,48,60,136,143,144] osmium,[81,82,84,87] cobalt,[153,154] and rhodium catalysts[33,156–158] has been described.

The ruthenium[60,70,136,138–140] and especially iron catalysts[33,40,45,47–49,55,127–137] are characterised by high selectivity in relation to the formation of lower olefins. These systems apparently possess a lower hydrogenating capacity, so that under the conditions of the synthesis the olefins formed initially are not hydrogenated to the corresponding alkanes. In the presence of these systems, there is no significant chain growth either.

Methanol and ethanol has been obtained only in the presence of rhodium[153,156–159] and iridium catalysts.[157]

High-molecular-weight hydrocarbons are formed from CO and H_2 only in the presence of cobalt systems,[90–92,94,96,145–152] which indicates the predominance of the hydrocarbon chain propagation stage over the termination stage in this instance.

Thus metal carbonyl catalytic systems for the specific synthesis of lower olefins, alcohols, or high-molecular-weight hydrocarbon from CO and H_2 have been most thoroughly developed and investigated. These catalysts can also be treated from a practical standpoint. The manufacture of iron and cobalt carbonyls has been achieved on an industrial

scale, which leads to prospects for the use of metal carbonyl systems based on them (with a low metal content) for the creation of stable and effective catalysts of synthesis from CO and H_2.

The fact that the systems are convenient for the investigation of the mechanisms of the syntheses of organic compounds from CO and H_2 and also of the influence of the composition and structure of the catalyst on its catalytic properties and for the elucidation of the nature and structure of the active centre for the synthesis is also fairly important.

Thus one may expect that in the future studies on the metal carbonyl catalysts of the synthesis of chemical products from CO and H_2 will continue.

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Reactions of Free Radicals with Organic Cations

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The kinetics and mechanisms of the reactions of organic cations of different types with neutral radicals, radical-anions, and radical-cations are considered and the dependences of the rates of these reactions on the nature of the substituents in the reactants, the charges on the radicals, the nature of the solvents and counterions, and the presence of crown ethers are analysed. The applications of the reactions of cations with radicals in the alkylation and arylation of organic compounds, in diazotypes, and in cationic and radical polymerisation are briefly surveyed.
The bibliography includes 128 references.

CONTENTS

I. Introduction 29
II. Reactions with diazonium cations 29
III. Reactions with the onium cations of Group V-VII elements 33
IV. Reactions with carbonium ions 35
V. Reactions with the cations of heteroaromatic compounds 36
VI. Conclusion 37

I. INTRODUCTION

As early as the beginning of the 1940's, the interaction of free radicals with diazonium cations was postulated[1,2] to account for the formation of azobenzenes in the reduction of diazonium salts. It was later established that the dediazotisation processes in methanol,[3-10] hypophosphorous acid,[11,12] and cyclic ethers[13,14] proceed via a radical-chain mechanism and that diazonium cations interact with radicals in the chain propagation and termination stages. Subsequent studies showed that the reactions of radicals with organic cations are very common in organic chemistry and are important in organic synthesis, in the electrochemistry of organic compounds, in polymer chemistry, and in diazotypes. Their kinetics and mechanisms have a number of characteristic features of general interest for the chemistry of organic cations and free radicals. The present review is devoted to the analysis and survey of the available literature data on the kinetics and mechanisms of the reactions of organic cations with neutral radicals, radical-anions, and radical-cations and their practical applications.

II. REACTIONS WITH DIAZONIUM CATIONS

Reactions of radicals with diazonium cations have been most thoroughly investigated. Various processes involving the thermal, photochemical, and radiation-chemical reduction of these cations result in the formation of aryl radicals, which can interact with the initial cations or can abstract hydrogen atoms from solvent molecules, forming radicals which also react with the cations. It has been suggested that the attack by radicals can be directed to the aromatic nucleus of the cation or to the diazo-group. The reactions of the first type account for the formation of arylazobenzenes, for example, in the reduction of diazonium salts by potassium hexacyanoferrate(II) in water.[2] The following reaction mechanism has been proposed:[2]

$$RC_6H_4^{\cdot} + RC_6H_4N_2^{+} \rightarrow RC_6H_4C_6H_4(R)N_2^{+} \quad (1)$$

$$RC_6H_4C_6H_4(R)N_2^{+} + RC_6H_4^{\cdot} \xrightarrow{-H^{+}} RC_6H_4C_6H_3(R)N{=}N{-}C_6H_4R \quad (2)$$

Among the products of the chain reaction of methanol with p-$ClC_6H_4N_2^{+}BF_4^{-}$, initiated by γ-radiation in water, the isomers of dichlorobiphenyl were isolated.[15] The authors suggest that these are formed as a result of reactions of type (I) and subsequent reduction of the radical-cation and the elimination of nitrogen. The isotopic composition of the biphenyl, formed on treatment of $PhN_2^{+}Cl^{-}$ with an aqueous solution of alkali in deuteriated benzene, has been explained[16] on the basis of a reaction mechanism involving the addition of the phenyl radical to the aromatic nucleus of the diazonium ion as one of the stages. However, we may note that the attack by radicals on the aromatic nucleus of the diazonium cation has not been unambiguously demonstrated, as the products of the above reactions can also be obtained in a different way.

The attack by the radicals on the diazo-group, i.e.

$$Ar^{\cdot} + ArN_2^{+} \rightarrow ArN{=}NAr^{+} \xrightarrow{e^{-}} ArN{=}NAr \quad (3)$$

has been proposed by Waters[1] to account for the formation of symmetrical azobenzenes in the Sandmeyer reaction. However, these azo-compounds can be obtained as a result of the recombination of aryl and diazenyl radicals and direct evidence for the formation of the radical-cations derived from azo-compounds was not obtained in Waters' studies.

Such evidence was obtained appreciably later in the study of the EPR spectra of the products of the benzenediazonium cation with sodium dithionate.[17,18] The authors observed in the EPR spectrum a quintet corresponding to the interaction of the unpaired electron with two equivalent nitrogen nuclei ($a_{N(1)} = a_{N(2)} = 9.2$ G). The g-factor for the radical was 2.0035. The observed spectrum was initially erroneously attributed to the diazenyl radical $C_6H_5N_2$. However, quantum-chemical calculation for the latter demonstrated[19] that it is a σ-radical in the ground state and that its nitrogen atoms are non-equivalent: $a_{N(1)} = 5.8$ G and $a_{N(2)} = 14.6$ G. This result agrees well with the hyperfine interaction (HFI) constants for diazenyl radicals obtained on decomposition of benzeneazoalkanes. It has been concluded[19] that the EPR spectrum obtained in the earlier studies[17,18] corresponds to the azobenzene radical-cation, since the calculated[19] and experimental[17,19] HFI constants for the nitrogen atoms in this radical-cation were found to agree.

On the basis of the dependence of the radiation-chemical yield in the consumption of the salt p-$CH_3C_6H_4N_2^{+}BF_4^{-}$ on its concentration in the chain decomposition process initiated by γ-radiation in aqueous methanol solution, it has been suggested[15] that chain termination proceeds via reaction (3) and the rate constant for this reaction was calculated ($k = 4.2 \times 10^6$ litre mol^{-1} s^{-1}).

It has been suggested[19] that not only aryl but also many other radicals can react via mechanism (3). The first evidence for this was obtained in relation to the radicals generated by the abstraction of hydrogen atoms from β-carbon atoms in alcohols or aldehydes by aryl radicals in the chain decomposition reaction of p-$CH_3C_6H_4N_2^+BF_4^-$ initiated by γ-radiation in aqueous solutions of ethanol, isopropyl alcohol, or aldehydes (RH_2). The reaction rate constants were determined from kinetic data:

$$\beta\text{-}RH^{\cdot} + p\text{-}CH_3C_6H_4N_2^+ \rightarrow p\text{-}CH_3C_6H_4N{=}N{-}\beta\text{-}RH^+ \qquad (4)$$

They proved to be 1.1×10^4 and 3.8×10^4 litre mol^{-1} s^{-1} for the radicals $HOCH_2CH_2^{\cdot}$ and $HOCH(CH_3)CH_2^{\cdot}$ respectively.[20]

The influence of substituents in the nucleus of the diazonium cation on the rate of reaction (4) with β-radicals of isopropyl alcohol has been investigated.[15] It was found that the values of $\lg k_4$ are correlated with the σ^+ constants of the substituents in the cation: $\rho_+ = -0.5$ for the substituents p-CH_3O, p-CH_3, and p-Cl, while the inclusion of p-CN and p-NO_2 in this series lowers ρ_+ to −1.0. The acceleration of the reaction following an increase in the electron-donating capacity of the substituent has been explained[15] by the stabilisation of the electron-deficient radical-cation when substituents are introduced into the nucleus.

By analogy with the azo-coupling reaction, the addition of radicals to the diazo-group and subsequent reduction of the radical-cations to neutral azo-compounds were called the free-radical azo-coupling reaction.[21-23] This reaction became a convenient method of synthesis of alkylaryldiazenes, especially those with tertiary alkyl residues:

$$R^{\cdot} + ArN_2^+ \rightarrow R{-}N{=}N{-}Ar^+ \xrightarrow{M^{n+}} R{-}N{=}N{-}Ar + M^{(n+1)+}$$
$$M^{n+} = Ti^{3+},\ Fe^{2+} \qquad (5)$$

The radicals $R^{\cdot}$ are generated either in the reactions of aryl radicals with alkyl iodides or in the reactions of ketones or dialkyl sulphoxides with hydrogen peroxide in the presence of iron(II) salts. The yield of azo-compounds is 30–80% of theoretical depending on the nature of $R^{\cdot}$.

The rate constants for the addition of radicals to diazonium cations have been estimated[22] at 0 °C in methanol: $k_5 \cong 10^6$ litre mol^{-1} s^{-1} for $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$ and $k \geqslant 10^8$ litre mol^{-1} s^{-1} for $(CH_3)_3C^{\cdot}$. This addition is reversible, since high yields of azo-compounds are obtained solely in the presence of relatively high concentrations of metal salts, which reduce the intermediate radical-cation and therby shift the equilibrium towards the final product. According to the authors of two investigations,[21,22] the addition of alkyl radicals to the diazonium cations is significantly accelerated if the degree of charge transfer from the radical to the cation in the transition state of reaction (5) increases. However, this hypothesis conflicts with the acceleration mentioned above, of the addition of isopropyl alcohol β-radicals under the influence of electron-donating substituents in the nucleus of the cation, since evidently the degree of charge transfer from the radical to the cation should fall with increase in the electron-donating capacity of the substituents.

Yet another common and thoroughly investigated type of reactions of radicals with diazonium cations involves electron transfer from the radicals to the cations:

$$R^{\cdot} + ArN_2^+ \rightarrow R^+ + ArN_2^{\cdot} \qquad (6)$$

It has sometimes been suggested (see, for example, Bargon and Seifert[19]) that these reactions proceed in two stages—with the intermediate formation and subsequent decomposition of the radical-cations $Ar{-}N{=}N{-}R^+$.

Evidence for the single-stage course of the reduction of diazonium cations with α-radicals derived from benzyl alcohol has been obtained[15,24] from data on the kinetics of the chain decomposition of diazonium salts initiated by γ-radiation in aqueous solution of the alcohol. Electron transfer from these radicals to the diazonium cations is the rate-limiting chain propagation step in the chain process. It has been found that the $\lg k$ for these reactions are correlated with the σ^+ constants of the substituents in the diazonium cations and that $\rho^+ = 0.55$ (the reaction is accelerated by electron-accepting substituents). We may note that a positive value of ρ has been obtained also for the correlation of the half-wave potentials in the polarographic one-electron reduction of substituted diazonium salts in sulpholan with the σ constants of the substituents in these salts.[25] The above data agree with a single-stage mechanism of electron transfer from the benzyl alcohol α-radicals to the diazonium cations.

The acceleration of the reactions with increase in the electron-accepting capacity of the substituents in diazonium cations has been observed also for the interaction of these cations with the radicals $^{\cdot}CH_2OH$ and $(CH_3)_2^{\cdot}COH$ investigated by pulse radiolysis.[26] The rates of the reactions increase on passing from the primary to the tertiary radical, which agrees with the decrease in the oxidation potential of the radicals[27] and hence corresponds to the mechanism involving electron transfer from the radicals to the cations in the slow stage.

The kinetics and mechanisms of the reduction of diazonium salts by stable triarylverdazyl radicals have been studied.[28] The products of the one-electron oxidation of the radicals, namely the verdazylium cations, were obtained in 90–95% yield. The products of the reduction of the cations ArN_2^+, i.e. the diazenyl radicals $ArN_2^{\cdot}$, were identified with the aid of chemically induced dynamic nuclear polymerisation (CIDNP) of the benzene formed from $PhN_2^{\cdot}$. The choice between the mechanism involving direct electron transfer in the slow stage of the process and the mechanism involving the formation and subsequent homologous decomposition of the radical-cation derived from the azo-compound was made on the basis of kinetic data. The reactions investigated are of first order with respect to each reactant and their rate constants k, calculated from the kinetic curves for the destruction of the radicals and the curves for the accumulation of verdazylium cations, agree over a wide range of variation of k (from 10 to 10^5 mol^{-1} s^{-1}). These data show that, even if the radical-cation is formed in the intermediate stage of the reaction, its stationary concentration is low. The values of $\lg k$ for the reactions considered increase linearly with increase in the reduction potentials of the diazonium cations and with decrease in the oxidation potentials of the verdazyl radicals, which agrees with the mechanism involving direct electron transfer from the radical to the cation in the slow stage. It has also been found that the $\lg k$ for the reactions of the triphenylverdazyl radical with the p-t-butylbenzenediazonium cation in various aprotic solvents decrease with increase in the donor number of the solvent. This is probably associated with the decrease in the equilibrium constant for the formation of the complex, preceding the electron transfer between the reactants, with increase in the strength of the donor–acceptor bonds between the diazonium cation and solvent molecules.

Electron transfer from radicals to diazonium cations has been postulated in the chain propagation stages of many chain processes involving the decomposition of diazonium salts in solutions containing substrates such as alcohols,[3-10,15,20,24,29] ethers [dioxan and tetrahydrofuran (THF)],[13,14,30,31] hypophosphorous acid,[11,12,32-34] cysteine,[34] and 2,4,6-triphenyl-4H-pyran,[35] but the kinetics has been studied in only some of the investigations,[14,15,20,24,30-35] where it was postulated

that the chain propagation process consists in the abstraction of hydrogen atoms from the substrate molecules by aryl radicals or the β-radicals of the substrates and in electron transfer from the substrate radicals formed to the diazonium cations. If the rate of the first of these stages is higher than that of the second, then the rate of the process is limited by electron transfer from the radicals to the cations and chain termination takes place mainly on recombination of the substrate radicals. The increase in the electron-donating capacity of the radicals derived from substrates or in the electron-accepting capacity of diazonium cations can make the first stage rate-limiting and chain termination then occurs on interaction of the aryl radicals or the substrate β-radicals with the diazonium cation.

Since the rate constants for the abstraction of hydrogen atoms from the CH bonds by phenyl radicals are known[36,37] and the rate-limiting chain propagation stage can be found from the type of the overall kinetic equation for the chain process, the above considerations make it possible to estimate the upper or lower limit to the rate constants for reactions (6). Thus, in the hydroquinone-initiated decomposition of diazonium salts in aqueous dioxan, the rate-limiting chain propagation stage involves electron transfer from the dioxan radical to the diazonium cation and the rate constant for this process must be lower than that for the abstraction of the H$^{\cdot}$ atom from the dioxan molecule by the phenyl radical, i.e. lower than the value 4.8×10^6 litre mol^{-1} s^{-1} known from the literature.

We may note that in those cases where the rate-limiting chain propagation stage consists in electron transfer from the substrate radicals to the diazonium cations, a correlation is usually observed between the overall rate of the chain process and the σ constants of the substituents in the nucleus of the diazonium cation with a positive value of the constant ρ (see, for example, Rykova et al.[31]). In doubtful cases, this feature can serve for the confirmation of the nature of the rate-limiting chain propagation stage and for the estimation of the limits of the rate constants for reactions (6).

It has been established[38,39] that the interaction of stable nitroxy-radicals with diazonium salts leads to electron transfer from the radicals to the cations. When crystalline diazonium tetrafluoroborates or chlorides are added to liquid di-t-butyl nitroxide, nitrogen is evolved and immonium salts are formed.[38] The phenyl or *p*-nitrophenyl radicals formed in this reaction recombine with the initial nitroxy-radicals, affording *NN*-di-t-butyl-*O*-phenylhydroxylamine or *NN*-di-t-butyl-*O*-(4-nitrophenyl)hydroxylamine in yields up to 75%, while the 2,4-dinitrophenyl and 2,4,6-tribromophenyl radicals abstract hydrogen atoms from the t-butyl group of the nitroxy-radical, forming *m*-dinitrobenzene or 1,3,5-tribromobenzene in yields of 22 and 13% respectively. The appearance of aryl radicals in the reaction has been confirmed by the formation of substituted bromobenzenes in the presence of CBr_4.

Intramolecular cyclisation leading to fluorescence (the Pschorr reaction) is not observed in the interaction of nitroxy-radicals with diazotised 2-aminobenzophenone, hydrogen atoms being abstracted by the benzophenone radicals from the nitroxy-radicals.[38] However, it was shown later that the interaction of nitroxy-radicals with *o*-substituted diazonium salts in acetone leads to the expected products of the intramolecular cyclisation. These data confirm the radical mechanism of the version of the Pschorr reaction considered.

Electron transfer from radical-anions to diazonium cations is also very common, but its systematic study has begun relatively recently. Reactions of this type have been postulated in chain propagation stages of the decomposition of diazonium salts in alkaline media[7,34] and in aqueous solutions of hypophosphorous acid.[34] It has been assumed[11,12,32,33] that diazonium cations interact with the $H_2PO_4^{\cdot}$ radical in the chain propagation stages of the last reaction; however, it is more likely that the conjugate base of the neutral radical, namely the radical-anion $HPO_2^{\cdot-}$, actually reacts with the cations. This is indicated by the detection of the $HPO_2^{\cdot-}$ species from the characteristic EPR spectrum comprising a doublet (a = 484 G) of doublets (a = 90 G) with a g-factor of 2.0028 in the oxidation of hypophosphorous acid with hydrogen peroxide in the presence of Tl^{3+} ions at pH between 2 and 8, i.e. under conditions where the acid reacts with diazonium salts; under these conditions, the signal of the $H_2PO_2^{\cdot}$ radicals is absent.[40] When a mixture of the salt $PhN_2^+BF_4^-$ and a phenyl radical trapping agent (maleic acid) was added to the given mixture, EPR signals corresponding to $HPO_2^{\cdot-}$ and the adduct of Ph$^{\cdot}$ with maleic acid were identified. It has been suggested[40] that the reaction

$$PhN_2^+BF_4^- + HPO_3^{\cdot2-} + H_2O \rightarrow Ph^{\cdot} + N_2 + H_2PO_3^- + HBF_4$$

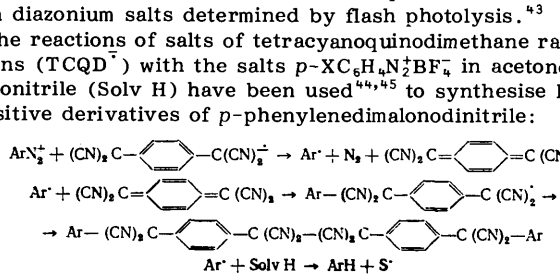
proceeds under these conditions.

The lower limit for the rate constant of the reaction of the diazonium cation with $HPO_2^{\cdot-}$ was found from chain kinetic data for the decomposition of p-$CH_3C_6H_4N_2^+BF_4^-$ initiated by γ-radiation in aqueous H_3PO_2 solution:[34] $k = 2.5 \times 10^6$ litre mol^{-1} s^{-1}. It was also shown in this study that the rate constant for the reaction of the diazonium cation with $HPO_2^{\cdot-}$ is lower than that for the reaction with the radical $^{\cdot}CH_2OH$, i.e. is smaller than 1.8×10^9 litre mol^{-1} s^{-1}.[25]

The rate constants for the interaction of substituted semiquinone radical-cations with substituted diazonium salts in water have been determined[26] by pulse radiolysis. It was found that the introduction of electron-accepting substituents into the aromatic nucleus of the diazonium cations and of electron-donating substituents into the semiquinone radical-anion accelerates the reaction, which agrees with the mechanism involving electron transfer from the radical-anions to the diazonium cations in the slow stage of the process. Comparison of the rate constants for the reactions of diazonium cations with the neutral radicals and radical-anions having identical oxidation potentials showed that the rate depends not only on the redox potential of the radical but also on its charge, since the interaction between ions of opposite charge lowers the activation energy and accelerates the reaction of radical-anions compared with neutral radicals.

The chain propagation stages of the synthetically important radical-chain arylation of quinones by a diazonium salt in aqueous solutions apparently involve the interaction of the diazonium cations with semiquinone radical-anions.[41,42] It has been suggested that complexes of the radical-anions with diazonium cations, having an absorption maximum at 380 nm, are formed in the slow stages of these reactions and then decompose rapidly with evolution of nitrogen. It has been found from overall kinetic data for the arylation process that the rate constant for the formation of the complex is 500 litre mol^{-1} s^{-1}. We may note that the value obtained is doubtful, since it is almost five orders of magnitude lower than the rate constants for the reactions of semiquinone radical-anions with diazonium salts determined by flash photolysis.[43]

The reactions of salts of tetracyanoquinodimethane radical-anions ($TCQD^{\cdot-}$) with the salts p-$XC_6H_4N_2^+BF_4^-$ in acetone or acetonitrile (Solv H) have been used[44,45] to synthesise light-sensitive derivatives of *p*-phenylenedimalonodinitrile:



A detailed study of the influence of the nature of the reactants and of the medium on the rate of reactions of this type has been undertaken.[46] Their kinetics are described by second-order equations—first order with respect to each reactant. The rate of reaction diminishes with decrease in the reduction potentials of the diazonium salts. It increases on passing from $TCQD^{\cdot}$ to the *p*-choranil radical-cation which has a higher oxidation potential than $TCQD^{\cdot}$. The dependence of lg *k* for the reactions of $PhN_2^+BF_4^-$ with $TCQD^{\cdot}$, with the *p*-chloronil radical-anion, and with a series of neutral verdazyl radicals in dimethyl sulphoxide on the oxidation potentials of the radicals is described by a single straight line. This indicates a small difference between the contributions of the electrostatic interaction to the free energy of activation by electron transfer from the radical-anions and neutral radicals to the diazonium cation. It has also been established that, in reactions involving electron transfer from radical-anions and neutral radicals to diazonium cations, the selectivity of the reactions diminishes with increase in the reactivity of the radicals. As in the reaction of the diazonium cation with the triphenyl-verdazyl radical, the rate of reaction of the diazonium cation with $TCQD^{\cdot}$ diminishes with increase in the donor number of the aprotic solvent.

The rates of reaction of diazonium salts with the radical-anion salts may be influenced also by the nature of the cation in the latter.[47] Thus in acetonitrile the rate of reaction of $p\text{-}(CH_3)_2NC_6H_4N_2^+BF_4^-$ with the $TCQD^{\cdot}$ radical-anion salts is independent of the nature of the cation M^+ in these salts, while the rates of the reactions in methanol decrease with increase in the ionic radius of M^+. These data have been explained by the fact that in acetonitrile the radical-anion salts exist in the form of solvate-separated ion pairs or free ions, while in methanol the equilibrium between the solvate-separated ion pairs and the less reactive close ion pairs is displaced appreciably towards the latter with increase in the radius of M^+.

The photodecomposition of diazonium salts served as the basis for diazoprinting processes (the production of diazotypes). It has been suggested that in the presence of quinones these reactions involve the interaction of diazonium cations with semiquinone radicals or radical-anions. The kinetics of these processes in aqueous acetonitrile solutions has been investigated.[48] The semiquinone radicals were generated by the interaction of triplet-excited 1,4-benzoquinone with 2,6-di-t-butyl-4-methylphenol. It has been shown that the rates of reaction increase with increase in the electron-accepting capacity of substituents in the aromatic nucleus of the cation and that the pH of the solution, on which depends the ratio of the concentrations of the neutral semiquinone radicals $QH^{\cdot}$ and the radical-anions $Q^{\cdot-}$, formed on acid dissociation of $QH^{\cdot}$, has an appreciable influence on the rate. Thus the rate constants for the reaction of $p\text{-}NO_2.C_6H_4N_2^+BF_4^-$ falls from 2.8×10^8 litre mol^{-1} s^{-1} to 2.9×10^5 litre mol^{-1} s^{-1} as the pH falls from 2.8 to −0.7.

The photochemical reactions of semiquinone radicals of different nature with diazonium salts in heptane, acetonitrile, and a mixture of acetonitrile and water have been investigated.[43] The radical species $QH^{\cdot}$ and $Q^{\cdot-}$ participants in two main processes: disproportionation into Q and QH_2 (or Q and Q^{2-}) and electron transfer to the diazonium ions. The rate constants for electron transfer from the radicals $QH^{\cdot}$ (k_e) and the radical-anions $Q^{\cdot-}$ ($k_{\bar{e}}$) to the salt $p\text{-}ClC_6H_4N_2^+.BF_4^-$ have been determined by flash photolysis. The constants k_e and $k_{\bar{e}}$ increase with decrease in the reduction potentials of the initial quinones Q, which agrees with the mechanism involving electron transfer from the radical to the cation. The values of $k_{\bar{e}}$ are higher than those of k_e by 2–3 orders of magnitude, which indicates a higher reactivity of the radical-anions compared with the neutral radicals. The rate constants for the disproportionation of $QH^{\cdot}$ and $Q^{\cdot-}$ in the media investigated have also been determined. It follows from the data obtained that the electron transfer to diazonium cations with weak electron-accepting substituents can compete in terms of rate with the disproportionation of only the $Q^{\cdot-}$ species present in appreciable concentrations only at high pH of the solution. However, as noted by Becker et al.,[43] in diazoprinting practice the pH of the medium does not exceed 3 and $QH^{\cdot}$ are the main species present in the system. Electron transfer to the diazonium salts containing only highly electron-accepting substituents in the nucleus can compete with the disproportionation of $QH^{\cdot}$.

The photochemical reduction of diazonium salts can proceed via the mechanism involving direct electron transfer to the cation from the sensitiser in an excited state or from the photochemically generated radical in the ground state. In the reactions of diazonium salts with the radicals derived from semiquinones corresponding to thionine or Methylene Blue, it was possible to distinguish these mechanisms. It was found that the direct electron transfer from the sensitiser in the excited triplet state to the cation proceeds with a low efficiency.[49]

The kinetics of the radical-chain photodecomposition of diazonium salts, sensitised by derivatives of anthraquinone or benzoquinone, in aqueous solutions of alcohols, sodium formate, sodium oxalate, and ethylenediaminetetraacetate (EDTA) and in poly(vinyl alcohol) matrices has been investigated.[50–53] The reaction mechanism proposed by the authors had been known previously for the decomposition of salts in alcohols and ethers.[14,15] When an aqueous ethanol is replaced by 0.1 M aqueous solutions of sodium formate, sodium oxalate, and EDTA, the chain length changes and amounts to 500, 4 and 15 respectively instead of 50 in ethanol. When the reaction is carried out in the polymer matrix in the presence of sodium formate, the chain length diminishes to 4. In order to diminish the rigidity of the polymer matrix and to facilitate the development of the dye-sensitised chain photodecomposition reactions of diazonium salts, plasticisers are introduced into the matrix.[54] It has been established that oxygen serves as a trapping agent for radicals and diminishes the chain length.

It has been shown[55] that diazonium cations quench the fluorescence of the triplet-excited anthracene and certain other hydrocarbons via the electron transfer mechanism with formation of hydrocarbon radical-cations in yields close to 100%. A number of other sensitisers in the triplet state transmit energy to the diazonium cations and the excited cations then decompose via a heterolytic mechanism with formation of aryl cations. The homolytic reaction pathway is characteristic only of triplets with a relatively low excitation energy and a high electron-donating capacity.

It has been shown[56] that the biradicals formed on photodissociation of γ-methylvalerophenone can also serve as the initiator of the chain decomposition of diazonium cations in methanol. The chain length in this process is 25. It has been established[57] by EPR that neutral radicals are formed in the photochemical reduction of riboflavin or protonated riboflavin cations in poly(ethylene glycol) films and interact with diazonium cations, initiating the chain process. In aqueous poly(ethylene glycol) solution, the chain length is close to 400, whilst in films it falls to 40. The application of the above initiators makes it possible to shift the region of the spectral sensitivity of diazo-materials to 500 nm.

The photosensitised deocomposition of diazonium salts in micellar solutions has been studied.[58–60] In the case of a surfactant forming negatively charged micelles (sodium dodecasulphonate), dynamic (with $k_d = 8.6 \times 10^{10}$ litre

mol^{-1} s^{-1}) and static (with K_{ass} = 210 mol $litre^{-1}$) quenching of the fluorescence of anthracene by added p-$CH_3C_6H_4N_2^+BF_4^-$ is observed. In the case of a compound giving rise to positively charged micelles (dodecyltrimethylammonium chloride), the efficiency of the dynamic quenching fell ($k_d = 1.9 \times 10^9$ litre mol^{-1} s^{-1}) and static quenching was not observed at all. It was concluded[60] that the efficiency of the quenching is determined mainly by the Coulombic interaction of the charges of the micelle and the quenching agent.

It has been shown[61,62] that the rates of the reactions of ketyl radicals, generated on photoirradiation of α-phenylbenzoin, with p-$ClC_6H_4N_2^+BF_4^-$ increase with increasing fraction of the excited radicals, which is associated with the decrease in the free energy of the electron transfer reactions on excitation.

A study has been devoted to the solution of the problem whether or not the photosensitised decomposition of diazonium salts in the presence of aromatic ketones proceeds via the electron transfer or the energy transfer mechanism.[63] It was demonstrated by the CIDNP method that diazonium salts decompose via the mechanism involving electron transfer from the excited ketones in the T_1 state to the diazonium cations with rate constants of (1.0–9.8) × 10^9 litre mol^{-1} s^{-1}. In the reactions of fluorenone and pyrene with the cations, the electron is transferred from these compounds in the S_1 state, which is most stable.

The data described facilitate the search for diazoprinting compositions incorporating diazonium salts and initiators, which decompose under the influence of light to radicals which interact with the cation initiating their chain decomposition.[64]

Aryl radicals and cations derived from the initial radicals are formed in the reactions involving the reduction of diazonium cations by radicals. These active species can initiate the radical and cationic polymerisation. The use of such systems for photopolymerisation is particularly promising. A system consisting of a photoinitiator (a benzoin ether or potassium oxalatoferrate) and a coinitiator (bisdiazonium salts) has been proposed[65] for the initiation of radical photopolymerisation. It was shown that the bisdiazonium salts induce the photopolymerisation of acrylamide at the same rate as diazonium salts but afford polymers with twice as high a molecular weight. The increase in the molecular weight of polyacrylamide was explained by the fact that in the case of bisdiazonium salts the products of the polymer chain termination contain diazonium groups capable of initiating further polymerisation.

The chain decomposition of diazonium salts can occur on transfer to the latter of an electron from the radical-anions $CO_2^{\cdot-}$ formed on photoirradiation of the complex oxalates $K_3[Fe(Ox)_3]$ and $K_3[Co(Ox)_3]$ at the wavelength of the charge transfer band.[66] The quantum yields in the evolution of nitrogen increase with increasing electron-accepting capacity of the substituents in the diazonium cations. Such systems are effective initiators of the photopolymerisation of acrylamide in the spectral range 400–500 nm.[67] The quantum yield of the photopolymerisation reaches 805 in the case of potassium trisoxalatocobaltate and the p-methoxybenzenediazonium salt.[68]

Systems comprising derivatives of benzoin and diazonium salts have been used to initiate the photopolymerisation of glycidyl isobutyl ether. It was established that the rate of polymerisation increases with increase in the electron-accepting capacity of the substituents in the cation and also in the following series of counterions associated with the p-$ClC_6H_4N_2^+$ cation: $BF_4^- < SbF_6^- < BF_6^-$.[69] Photopolymerising layers for the preparation of relief images in the manufacture of printing plates or recording materials have been proposed on the basis of systems consisting of diazonium salts, oligomers, and photoinitiators (benzoic acid esters[70] or aromatic carbonyl compounds[71]).

It has been established[72] that the reduction of substituted diazonium salts by tetra-t-butylbispyrylium, tetramethyl-p-phenylenediamine ($TMPA^{+\cdot}$), tetraphenylbenzidine, and *N*-methylphenothiazine radical-cations obeys a second-order equation and proceeds via the electron transfer mechanism. The logarithms of the rate constants for these reactions decrease linearly with increase in the standard free energy of electron transfer. The rate of reaction of $PhN_2^+BF_4^-$ with $TMPA^+$ and the selectivity in the reduction of substituted diazonium salts by $TMPA^{+\cdot}$ increase with increase in the electron-donating capacity of the solvent. The addition of crown ethers to the solution accelerates the reaction. The rate increases also with increase in the ionic strength of the solution, Cl^- ions exhibiting a specific accelerating effect. These features of the influence of the medium are the opposite of those in the reactions of organic cations with neutral radicals[28] and with radical-anions.[46] They have been explained[72] by the fact that electron transfer takes place in "bridged" complexes incorporating solvent with crown ether molecules or the Cl^- anion, distributed between the organic cation and the radical-cation. The formation of a "bridge" lowers the electrostatic repulsion between the cation and the radical-cation, brings them closer together, and accelerates the reactions. The magnitude of the effect is determined by the electron-donating capacity and polarisability of the "bridged" molecules. In contrast to this, the reduction of organic cations by neutral radicals or radical-anions requires the desolvation of the reactants and the formation of an ion–dipole complex or a close ion pair in which electron transfer actually takes place.[47]

III. REACTIONS WITH THE ONIUM CATIONS OF GROUP V–VII ELEMENTS

Various thermal and photochemical reduction reactions of iodonium and sulphonium salts as well as the reduction reactions of diazonium salts proceed via a radical-chain pathway. Electron transfer from the chain propagating radical to the onium cations has been postulated in the chain propagation stages of these reactions. It has been shown[73–75] on the basis of kinetic data and observations of CIDNP effects of the products that the reactions of diphenyliodonium chloride with dibutylamine, monoethanolamine, and triethylamine proceed via this mechanism. In the reaction with dibutylamine, the rate-limiting chain propagation stage is electron transfer from the dibutylaminyl radical to the cation. In contrast to this, the rate-limiting chain propagation stage in the interaction of iodonium cations with monoethanolamine and triethylamine is abstraction of hydrogen atoms from the amine by phenyl radicals. The differences between the nature of the rate-limiting stages have been attributed[75] to the fact that the radicals $(C_2H_5)_2N\dot{C}HCH_3$ or $\dot{N}HCH_2CH_2OH$ are less stable than $(C_4H_9)_2N^{\cdot}$; the rate of formation of the first two radicals is therefore reduced, which makes the process rate-limiting.

The interaction of alcohol α-radicals with onium cations has been postulated during the chain propagation stages of the reactions of diaryliodonium cations with 2-nitropropane anions in methanol[76] and also in the reactions involving the decomposition of iodonium[77,78] and sulphonium[79] salts by sodium alkoxides in alcohols. It has been suggested[79] that the reaction with sulphonium cations leads to the formation of radical-cations of the type $R_3S^{+\cdot}$–$C(OH)(CH_3)_2$, but the nature of the

products formed can also be accounted for by electron transfer from the alcohol α-radical to the sulphonium cation.

The kinetics of the reduction of iodonium salts and onium salts of Group VI elements by stable verdazyl radicals and tetracyanoquinodimethane and *p*-chloranil radical-anions has been investigated.[80] It follows from the kinetic data obtained that the diphenyliodonium cation is a much weaker electron acceptor than diazonium ions. However, when the phenyl residue in the iodonium cation is replaced by the perfluoroalkyl residue, the rates of reactions with radicals increase sharply. For iodonium and sulphonium salts, they depend on the inductive effects of the substituents at the central atom and decrease in the following sequence: $n\text{-}C_6F_{13} > n\text{-}C_3F_7 \gg Ph > CH_3$.

The rates of the reactions of the onium cations of Group VI elements with the verdazyl radical in acetonitrile increase with increase in the principal quantum number of the central atom—in the sequence S < Se < Te. The half-wave potentials for the irreversible one-electron polarographic reduction of the cations in acetonitrile increase in the same direction. This finding has been explained by the fact that, in the transition states of the reaction considered, the bond between the central atom and the carbon atom of the substituent is appreciably weakened. The strength of this bond falls with increase in the principal quantum number of the central atom. This lowers the standard free energy and the energy of the reorganisation reactions in the above series and increases the rate.[81] An analogous behaviour has been observed in the series of isotypical onium cations of Group V and VII elements with alkyl and aryl substituents at the central atom. The ease of their irreversible polarographic reduction increases in the following series of cations: ammonium < phosphonium < arsonium,[82] chloronium < bromonium < iodonium.[83] The explanation of this feature is analogous to that quoted above.[81]

Processes in which onium salts undergo one-electron reduction have been used to generate alkyl or aryl radicals. The study of the products of the reduction of sulphonium salts of different structure by graphite or naphthalene radical-anions in tetrahydrofuran led Beak and Sullivan[84] to the following reaction mechanism:

$$RR'R''S^+ \xrightarrow{e^-} RR'R''S^\cdot \rightarrow R^\cdot + R'SR'' .$$

The selectivity of the bond dissociation in the radical $RR'R''S^\cdot$ depends on the nature of the residues R and in the reduction of monophenylsulphonium salts diminishes in the following sequence of R: benzyl > s-alkyl > n-alkyl > methyl > phenyl. It has been suggested that an electron is transferred in the first stage of the reaction from the radical-anion to the phenyl residue of the sulphonium cation and a π-ligand radical-anion associated with the sulphonium cation is formed. This species then decomposes into a sulphide and a hydrocarbon radical, it being assumed that the transition state of the decomposition process involves the overlap of a singly occupied molecular orbital of the aromatic nucleus with the σ* orbital of the homolytically dissociating bond. The selectivity of the decomposition is determined mainly by the relative energies of the radicals formed, although it is also influenced by steric factors. Alkylsulphonium cations are not reduced by the radical-anions employed, since the energy of their highest occupied molecular orbital is much higher than for the phenyl-substituted salts.

Another mechanism of the reduction of sulphonium salts, involving a synchronous electron transfer and the dissociation of the S–R bond, has been proposed.[85] It is based on the observed high sensitivity of the peak potentials on the voltage–current curves for the electrochemical reduction of phenyl- and naphthyl-dialkylsulphonium salts to the electron-accepting capacity of the leading group, which determines the relative energy of the σ* molecular orbital of the bond ruptured on reduction.

The nature of the radicals formed in the electrochemical reduction of sulphonium cations in the presence of radical trapping agents (nitrosodurene, t-butyl phenyl nitrone) has been investigated by the cyclic voltamperometric and coulometric methods at a constant potential with recording of the intermediate products by EPR.[86] In certain cases difficulties arose, associated with the greater ease of the reduction of the trapping agents than of the cations. They were overcome by using the indirect homogeneous reduction of the cations by redox catalysts (anthracene, 1,8-dinitronaphthalene), whose electrochemical reduction occurs at more positive potentials than the reduction of the trapping agents. Under these conditions, the radical-anions formed from the catalysts do not reduce the trapping agent but do reduce the sulphonium cations, being themselves oxidised to the initial hydrocarbons.

A preparative study of the products of the electrochemical reduction of sulphonium and butyltrimethylammonium salts, carried out using electron transferring agents such as fluorene and *p*-cyanoaniline, showed that alkylated derivatives of the transferring agents are formed with a high current yield.[87] In this connection, we may point out that the reactions of onium salts with electrochemically generated radical-anions[88,89] or radical-dianions[90] can serve as a convenient method for the alkylation or arylation of organic compounds formed on oxidation of these radical-anions. The reactions of tetraalkylammonium salts with the electrochemically generated triphenylphosphine or triphenylphosphine oxide radical-anions lead to the exchange of the organic residues linked to the phosphorus:[89]

$$Ph_3P \xrightarrow{e^-} Ph_3P^{\cdot-}$$
$$Ph_3P^{\cdot-} + (C_4H_9)_4N^+ \rightarrow [Ph_3PN(C_4H_9)_4]^\cdot$$
$$[Ph_3PN(C_4H_9)_4] \rightarrow C_4H_9\dot{P}Ph_3 + (C_4H_9)_3N$$
$$C_4H_9\dot{P}Ph_3 \rightarrow Ph^\cdot + C_4H_9PPh_2$$
$$C_4H_9PPh_3 \rightarrow C_4H_9^\cdot + Ph_3P .$$

The possibility of the reactions of electrochemically generated neutral radicals and radical-anions with onium cations, usually employed as supporting electrolytes in electrochemical synthesis in aprotic solvents of low polarity, must be taken into account in the reduction of organic compounds at high cathodic potentials. Thus, in the electrochemical reduction of benzonitrile in a solution of a tetraethylammonium salt, a reaction of the type of Hofmann degradation of the tetraalkylammonium cation by the benzonitrile radical-anion takes place.[91] It has been found that the rate of disappearance of the radical-anion increases linearly with increasing concentration of the ammonium salt.

In reactions with onium cations, the radical-anions can serve either as donors of one electron or as nucleophiles. In order to elucidate the relative contributions of these types of reaction of the benzophenone radical-anion, use was made of the aryltrimethylammonium salts, which give rise to N–Ar bond dissociation products in one-electron reduction and to products of the rupture of the $N-CH_3$ bonds following the attack by nucleophiles.[92,93] It was found that the above ratio is 2:3 for the reaction of $(C_6H_5)_2CO^-K^+$ with $C_6H_5N^+(CH_3)_3ClO_4^-$ in THF.[93] It increases with increase in the electron-accepting capacity of the substituents in the aromatic nucleus of the ammonium cation. When the nature of the counterion in the radical-anion salt is varied, the contribution of the nucleophilic substitution diminishes in the sequence $K^+ > Na^+ > Li^+$. These data[93] led to the conclusion

that the nucleophilic substitution process is more sensitive to the nature of the counterion M^+ in the radical-anion salt than the electron transfer process and that the latter is more sensitive to the structure of the electrophile than nucleophilic substitution.[92]

Yet another type of reaction with ammonium cations is characteristic of radicals having pronounced electrophilic properties ($Cl_2^{\cdot-}$, $HPO_4^{\cdot-}$, $SO_4^{\cdot-}$, $OH^{\cdot}$), which abstract hydrogen atoms from the alkyl substituents of the cation. The rates of reaction increase with increase in the number of C–H bonds in the alkyl residues and the relative reactivity of the radicals increases in the sequence $Cl_2^{\cdot-} < HPO_4^{\cdot-} < SO_4^{\cdot-} < OH^{\cdot}$, which is identical with the series based on the relative reactivities of the radicals in processes involving the abstraction of a hydrogen atom from other aliphatic compounds. The data described show that the reactions of radicals with ammonium cations involve the abstraction of $H^{\cdot}$ atoms in the rate-limiting stage. The influence of the positively charged nitrogen atom is manifested by a decrease in the rate constant for the abstraction of $H^{\cdot}$ from the α-carbon atom by two orders of magnitude and from the β-carbon atom by a factor of five compared with the rate constant for the abstraction of $H^{\cdot}$ from aliphatic hydrocarbons.[94]

A series of studies[95–98] have dealt with the influence of added diazonium, iodonium, and sulphonium salts on the yields and molecular weights of the polymers formed in the thermal or photochemical cationic polymerisation of alkyl vinyl ethers or THF. It was found that in the presence of sources of radicals (azobisisobutyronitrile, benzoyl peroxide) but in the absence of onium salts, the thermal polymerisation of these monomers does not occur, as happens also in solutions of the onium salts in the monomers. However, polymerisation does take place when both a radical initiator and an onium salt are added simultaneously to the solution. The following mechanisms of the formation of cations (polymerisation initiators) have been proposed:

$$X^{\cdot} + CH_2{=}CHOR \rightarrow X{-}CH_2\dot{C}HOR\,,$$
$$\sim\!-CH_2\dot{C}HOR + Ar_2I^+ \rightarrow \sim\!-CH_2CH{=}\overset{+}{O}{-}R + ArI + Ar^{\cdot},$$
$$Ar^{\cdot} + CH_2{=}CHOR \rightarrow ArCH_2\dot{C}HOR\,,$$
$$ArCH_2\dot{C}HOR + Ar_2I^+ \rightarrow ArCH_2,\ CH{=}\overset{+}{O}{-}R + ArI + Ar^{\cdot},$$
$$X^{\cdot} + \langle\!\rangle\!\!\rangle \rightarrow XH + \langle\!\rangle\!\!\rangle^{\cdot} \xrightarrow{Ar_2I^+} \langle\!\rangle\!\!\rangle^{+} + ArI + Ar^{\cdot}\,.$$

Here $X^{\cdot}$ is a radical derived from the initiator and $\sim\!-CH_2\dot{C}HOR$ is the macroradical. Evidently the role of the onium cations consists in the one-electron oxidation to carbonium ions of the radicals, formed with participation of the initiators or macroradicals. If these carbonium ions are unstable and decompose with elimination of protons, then the latter can also initiate polymerisation.

The method considered is especially effective in cationic photopolymerisation. Irradiation with hard ultraviolet light is necessary for the initiation in the absence of onium salts and the quantum yields are low, whereas in the presence of onium salts, the radical photoinitiators may be benzoin and its ethers or alkoxyacetophenones, which absorb light at wavelengths greater than 380 nm and decompose with high quantum yields. Detailed reviews[99,100] have been devoted to the development of initiating systems for photopolymerisation processes involving electron transfer to onium cations of different types from sensitisers in the excited state or from nucleophilic radicals formed on photolysis of benzoin derivatives and ketals and also on photoabstraction of hydrogen from aromatic ketones.

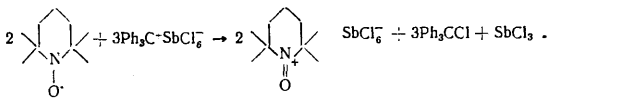
IV. REACTIONS WITH CARBONIUM IONS

The reactions of neutral radicals and radical-ions with carbonium ions have been postulated in the stages of certain radical processes involving carbonium ions, but there have been scarcely any quantitative studies of such processes. Two mechanisms of these reactions have been proposed—the one-electron reduction of the carbonium ion by the radical to the corresponding hydrocarbon radical or the recombination of the reactants.

The reactions in which triphenylcarbenium ions are reduced by a nitroxy-radical give rise to the stable triphenylmethyl radical; in the absence of atmospheric oxygen and water, an equilibrium displaced towards the initial reactants is established in organic solvents:

$$\rangle N{-}O^{\cdot} + Ph_3C^+ClO_4^- \rightleftarrows \rangle\overset{+}{N}{=}OClO_4^- + Ph_3C^{\cdot}\,.$$

In the presence of oxygen, which binds triphenylmethyl radicals, this equilibrium is wholly displaced to the right and triphenylmethyl peroxide, triphenylmethanol, and an immonium salt are formed. If $SbCl_6^-$ is the anion in the salt, then the anion and not the carbonium ion is reduced:[101]



In the reaction of $Ph_3C^+ClO_4^-$ with di-t-butyl nitroxide in the presence of oxygen, the peroxy-radical $Ph_3CO_2^{\cdot}$ has been shown[102] to abstract a hydrogen atom from the alkyl group of the nitroxide with formation of the hydroperoxide Ph_3CO_2H, the olefin $H_2C{=}C(CH_3)_2$, and the nitroso-compound $(CH_3)_3.CN{=}O$.

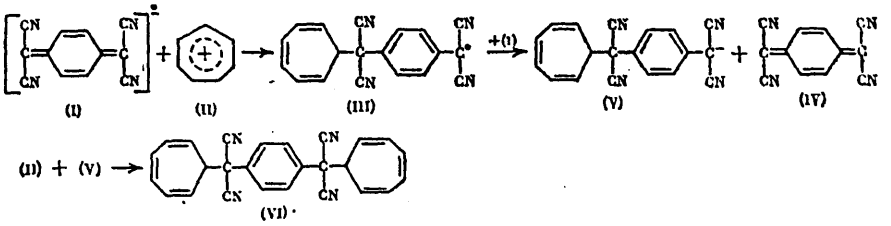
The formation of bitropyl in the reduction reactions of the tropylium cation may be the result of the recombination of tropyl radicals or of the attack by the tropyl radical on the tropylium cation and the subsequent reduction of the bitropyl radical-cation to a neutral compound. The latter mechanism has been proposed for the electrochemical reduction of tropylium (Tp^+) fluoroborate in acetonitrile, which leads to bitropyl:[103]

$$Tp^+ + e^- \rightarrow Tp^{\cdot},$$
$$Tp^+ + Tp^{\cdot} \rightarrow Tp_2^{\cdot+},$$
$$Tp_2^{\cdot+} + Tp^{\cdot} \rightarrow Tp_2 + Tp^+.$$

This mechanism is based on the agreement between the observed experimental slope of the polarographic reduction wave and the calculated slope for the mechanism quoted.

The reaction of tropylium fluoroborate with the oxygen radical-anion leads to benzene, benzaldehyde, cycloheptatriene, CO, and O_2.[104] It has been suggested that $O_2^{\cdot-}$ recombines with the cation in the first reaction stage. This is based on the ratio of the products of the reaction of the tropylium salt with a typical nucleophile—the O_2^{2-} anion, which does not differ from the ratio of the products of the reactions of the salts with $O_2^{\cdot-}$.

The interaction of the lithium salt of the tetracyanoquinodimethane radical-anion (I) with tropylium iodide (II) in acetonitrile affords tetracyanoquinodimethane (IV) and αα′α′-tetracyano-αα-ditropyl-p-xylene (VI). The following reaction mechanism has been proposed on the basis of the high yields of these products and the absence of bitropyl among them:[105]



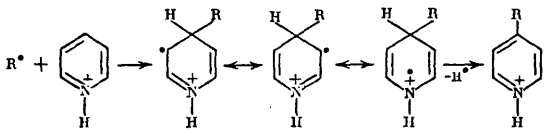
Here the radical-anion plays the role of the nucleophile. However, the product (IV) can also be formed as a result of the one-electron reduction of the cation (II) by the radical-anion (I). The reaction of compound (IV) with the tropyl radical (VII) formed simultaneously gives rise to the product (VI) if the rate of reaction of the species (IV) with (VII) is higher than the rate of dimerisation of the radicals (VII).

A mechanism of the last type, involving electron transfer from the radicals to the tropylium cation, has been proposed on the basis of kinetic data and the analysis of the products of the reactions of tropylium fluoroborate with substituted verdazyl radicals and tetracyanoquinodimethane or *p*-chloranil radical-anions.[106] It has been confirmed by the finding that the rates of these reactions increase with decrease in the oxidation potentials of the radicals and by the fact that the linear relation between the logarithms of the rate constants and the half-wave potentials for the polarographic reduction of the cations, which is characteristic of electron transfer reactions, has been observed for the reactions of the verdazyl radical with substituted diazonium, tropylium, and 2,4,6-triphenylpyrylium salts in acetonitrile.

In contrast to the reactions of diazonium cations with the triphenylverdazyl radical and with the tetracyanoquinodimethane radical-anion, whose rate diminishes with increase in the donor number of aprotic solvents,[28,46] the rate of reduction of the tropylium cation by the triphenylverdazyl radical depends only slightly on this parameter of the medium. This difference has been explained[106] by the fact that the increase in the degree of delocalisation of the charge on passing from the diazonium to the tropylium cation entails a decrease in the energy of the specific solvation of the tropylium cation by electron-donating solvents. As a consequence of the low specific solvation energy, the rates of the reactions of the tropylium cation with the radicals depend significantly on the non-specific solvation of the cation and the radical, so that $\lg k$ increases with increase in $1/\varepsilon$ (where ε is the dielectric constant of the medium). The rate of reaction of the tropylium cation with the tetracyanoquinodimethane radical-anion diminishes with increase in the polarisability of the solvent P, since an increase in P promotes the solvation of the readily polarisable radical-anion.

V. REACTIONS WITH THE CATIONS OF HETEROAROMATIC COMPOUNDS

The interaction of nucleophilic radicals with protonated heteroaromatic bases leads to homolytic substitution products, for example:



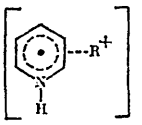
In recent years, reactions of this type have acquired synthetic importance.[107-111] Their rates are high and they exhibit a high positional selectivity and selectivity with respect to the substrate, in contrast to radical substitution reactions involving the molecules of neutral aromatic compounds, which are characterised by relatively low rates and positional selectivity and also by a weak sensitivity of the rate to the nature of the substituents in the aromatic nucleus. It has been suggested[112,113] that the principal cause of the above differences is appreciable polar effects in the reactions of the radicals with the cations. The transition state in these reactions is a charge-transfer complex and the degree of charge transfer is determined by the electron-donating capacity of the radical (the energy level of its singly occupied molecular orbital) and by the electron-accepting properties of the cations (the level of their lowest unoccupied molecular orbital).

The view described above has been confirmed by a number of observations. Thus the rates of the reactions of the heptyl radical with substituted pyridinium cations increase with increase in the electron-accepting capacity of the ring substituents, which is associated with a decrease in the activation energy for a constant pre-exponential factor. The activation energy falls and the rate and selectivity increase, because electron-accepting substituents stabilise the transition state corresponding to the electron transfer.[112]

It has been found[113] that the relative rates of homolytic substitution in the α-position in the rings of γ-substituted pyridines in an acid medium diminish with increase in the ionisation potential of the radicals (on passing from the benzyl to the phenyl radical) and also with increase in the σ constants of the substituents in the rings of the benzyl radicals.

We may note that the rule governing the correlation between the reactivity and selectivity, according to which an increase in the rates of reactions entails a decrease in their selectivity, breaks down in the cases considered. It has been suggested[112] that this rule does not hold at all in radical reactions with a highly polar transition state. However, it follows from certain data[26,46] that this rule does hold in reactions involving total electron transfer from radicals to diazonium cations.

The influence of the nature of the solvent on the kinetics of the reactions considered has been studied in relation to the bioxanyl, benzoyl, carbamoyl, α-aminomethyl, and undecyl radicals with protonated 4-cyano- and 4-methyl-quinolines.[114] An increase in the content of water in dioxan and also in the concentration of acetic acid in dioxan or in dimethylformamide increase the reaction selectivity. This has been explained by the interaction of water or acid molecules with the unshared electron pairs of the radicals, which increases the ionisation potential of the latter and diminishes the contribution by the form

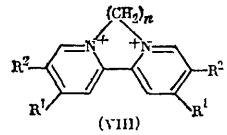


to the transition state. The reaction is thereby slowed down and its selectivity increases. We may note that this explanation does not take into account the change in the solvation of the cations and furthermore contradicts the increase in selectivity with increasing rates of the reactions considered discovered by Citterio et al.[112]

The limiting case of a polar transition state is observed in processes involving total electron transfer from the radical to the cation of the heteroaromatic compound. In such cases, electron transfer products are formed instead of the products of the addition of the radicals to the cations. Total electron transfer may be expected in the reactions of cations with nucleophilic radicals such as $(CH_3)_2\dot{C}OH$, $(C_6H_5)_2\dot{C}OH$, and $C_{10}H_8^{\cdot-}$. The study of the kinetics of the interaction of the radicals $(CH_3)_2\dot{C}OH$ with substituted pyridinium cations in water revealed a correlation between $\lg k$ and the σ constants of the substituents in the cation with the very high positive value $\rho = +8.5$.[115] This observation is a serious argument in support of a transition state close to a charge-transfer complex.

The formation of radicals from the cations of heteroaromatic compounds on their reduction by the photochemically generated radicals $(C_6H_5)_2\dot{C}OH$ or $C_{10}H_8^{\cdot-}$ has been demonstrated unambiguously by EPR.[116] The interaction of cations with classical ionic nucleophiles (OH^-, tertiary amines) leads to the same heteroaromatic radicals. It has been suggested[16] that in all the cases quoted an electron is transferred from the nuclophile to the electron-accepting cation.

The kinetics and the equilibrium in the reduction of dications having the general formula



(VIII)

where $n = 2-4$, $R^1 = H$ or CH_3, and $R^2 = H$ or CH_3, in their interaction with e_{aq}, $CO_2^{\cdot-}$, and $(CH_3)_2\dot{C}OH$ in water have been investigated by pulse radiolysis[117] and it has been found that the rates of the reactions with equated electrons are independent of the reduction potentials of the dications, while the rate of electron transfer from the radicals falls with decrease in these potentials. The rate constants for electron exchange between the radical $(CH_3)_2\dot{C}OH$ and protonated acetone and between the substituted pyrazinium bromide radical-cation and its unreduced form have been estimated from data derived from the equations of the theory of outer-sphere electron transfer reactions developed by Marcus. They proved to be $(2-6) \times 10^6$ litre mol^{-1} s^{-1} and 5×10^7 litre mol^{-1} s^{-1} respectively.

Irradiation of solutions of benzophenone or xanthone and *NN'*-dimethyldipyridinium dichloride (MB^{2+}) in aqueous isopropyl alcohol solution by light at a wavelength greater than 366 nm leads to the generation of the radical-cations $MB^{\cdot+}$ as a result of electron transfer to MB^{2+} from the photochemically generated ketyl radicals or from the alcohol α-radicals. The radical-cations reduce water with evolution of hydrogen, being reoxidised at the same time to the initial dications.[118,119] A significant increase in the quantum yield in the decomposition of water has been achieved by irradiating solutions of γ-ketoalcohols and MB^{2+} in aqueous acetonitrile solution by near ultraviolet light.[120] Thus the radicals $Ph\dot{C}(OH)CH_2.CH_2\dot{C}(OH)Ph$, which reduce MB^{2+} to $MB^{\cdot+}$ with a high rate constant [$(1-3) \times 10^8$ litre mol^{-1} s^{-1}] and a quantum yield of 0.7, have been generated in the system with $PhCH(OH)CH_2.CH_2COPh$.

The formation of the radical dimers in the electrochemical reduction of 3-ethyl-2-methylbenzothiazolium (BT^+) as well as the formation of bitropyl in the reduction of tropylium cations are treated as a result of the attack by the electrochemically generated radical on the initial cation:[121]

$$BT^+ \xrightarrow{e^-} BT^{\cdot},$$
$$BT^+ + BT^{\cdot} \rightarrow BT\text{-}BT^{\cdot+},$$
$$BT\text{-}BT^{\cdot+} \xrightarrow{e} BT\text{-}BT,$$
$$BT\text{-}BT^{\cdot+} + BT^{\cdot} \rightarrow BT\text{-}BT + BT^+.$$

The voltamperogram of the cation has two peaks. The first corresponds to a reversible process at a high rate of scanning of the potential, while the second peak corresponds to an irreversible process at all the rates of scanning of the potential investigated. The mechanism presented above was proposed on the basis of the dependence of the heights and potentials of both reduction waves for the cation on its concentration.

VI. CONCLUSION

In this Section we shall deal with certain general questions of the kinetics and mechanisms of the reactions considered. The data examined in the review show that the main types of reactions of organic cations with radicals involve the addition of the latter to the cations and electron transfer between these reactants. The reactions in which a hydrogen atom is abstracted from the C–H bonds of the hydrocarbon substituent of the cations are encountered much more rarely. They are characteristic of electrophilic radicals, for example, of $OH^{\cdot}$ and $SO_4^{\cdot-}$.

The presence of a charge on organic cations and the low energy of their lowest unoccupied molecular orbitals may be noted as characteristic features of the electronic structure of such species. The high electron affinities[122] and half-wave potentials for polarographic reduction[123] are related to these features. Since the majority of the radicals considered in this review are nucleophilic in character, one can assume that the main factors determining the direction and energetics of both addition and electron transfer reactions between radicals and cations are the Coulombic interaction between these species and the interaction of the singly occupied molecular orbital of the radicals, which have a high energy, with the lowest unoccupied orbital of the organic cations. The attack by the radicals should therefore be directed to the atoms of the cation having the minimum electron density. These conclusions are confirmed by data obtained for the recombination of cations of the type $H-C{=}O$ and $HO-\overset{+}{C}{=}O$, etc. with hydrogen atoms in the gas phase:[124] the activation energy for the addition of the $H^{\cdot}$ atom to the heteroatom is considerable, while the activation energy for the addition to carbon is low or zero.

The polar character of the transition state in the addition of electron transfer reactions considered is usually reflected by high positive values of the constants ρ in correlation equations linking the logarithms of the rate constants with the σ constants of the substituents in the aromatic nuclei of the cations[15,24,31,35,69,112,115] and the α constants in the equations relating the free energies of activation for the reactions to the free energies of electron transfer between the reactants.[125] The polar character of the transition state is also manifested by the acceleration of the reactions with increase in the electron-accepting capacity of the substituents in the cation[15,24,26,28,43,46,69,72,80,112,115] and in the electron-donating capacity of the radicals.[22,26,28,46,48,72,80,106,113,117] However, we may note that a negative value of ρ has been

obtained for the addition of isopropyl alcohol β-radicals to diazonium cations according to kinetic data for the chain radiolysis of diazonium salts in aqueous isopropyl alcohol.[15] This observation needs to be checked by a direct kinetic method.

A distinctive feature of the reactions involving the addition of radicals to cations investigated hitherto is the increase in selectivity with increase in the reactivity of the radicals or the cations,[112] while in the reactions involving electron transfer from the radicals to the cations the usual rule operates—the selectivity diminishes with increase in reactivity. The reactions involving the reduction of onium cations of Group VI elements by radicals are now known to be an exception to this rule.[81]

The rates of the reactions considered depend not only on the electron-donating capacity of the radicals and the electron-accepting capacity of the cations but also on the sign and magnitude of the charges on the radicals. For the reactions of neutral radicals with cations, the contribution of the ion–dipole interaction to the free energy of activation may be neglected, while for the interaction of radical-ions with cations this contribution is significant; for example, in acetic acid, for a distance between the reactants in the collision complex of 5 Å, this contribution is more than 40 kJ litre mol^{-1}.[126] In the reactions between radical-ions and large cations in media with a high dielectric constant, this contribution is reduced and in slow reactions is insignificant.[46] It increases, for example, with increase in the electron-donating capacity of radicals, leading to a sharp acceleration of the reactions.[26]

In contrast to the reactions involving electron transfer from the radicals to neutral organic compounds, in which the effects of the medium are determined by the solvation of the polar transition state,[127] in reactions involving electron transfer from the radical to the cations these effects are associated mainly with the solvation of the initial reactants. It has been shown for the reactions with electron transfer from neutral radicals, radical-anions, and radical-cations to the diazonium and tropylium cations[72,103] that the character of the influence of the nature of the solvents, of the added crown ethers, and of the nature of the counterions depends on the characteristic features of the structure of the organic cations and the charge on the radicals.

The kinetics of the reduction of organic cations by radicals can be described in terms of the theory of the outer-sphere electron transfer reactions developed by Marcus.[128] The rate constants k for more than 90 reduction reactions of diazonium, tropylium, verdazylium, and pyrylium cations with neutral radicals, radical-anions, and radical-cations as well as with diamagnetic organic molecules have been found[125] from the redox potentials of the reactants with the aid of the equations of this theory. It has been shown that, when account is taken of the energy of the reorganisation of only the outer coordination sphere, the calculated constants k exceed the experimental values by 1–7 orders of magnitude. Quantum-chemical calculations have shown that the reduction of the diazonium and tropylium cations to the corresponding radicals is accompanied by a significant change in structure, which leads to high energies of reorganisation of the inner coordination sphere of the cations in the reduction process. Calculation of the constants k taking this factor into account yielded a satisfactory agreement between the experimental and calculated values within the limits of 1–2 orders of magnitude.

It has been shown[125] that processes involving direct electron transfer to organic cations can be distinguished from processes in which electron transfer is preceded by the formation of an intermediate product of the recombination of the reactants with the aid of calculations based on the equations of the Marcus theory. Only for reactions of the first type is it possible to obtain a satisfactory agreement between the experimental constants k and the values calculated from the redox potentials of the reactants and the energies of the reorganisation reactions. For reactions of the second type, the experimental recombination rate constants exceed by many orders of magnitude the values calculated from the Marcus theory. This difference is greater the stronger the bond in the intermediate compound ruptured on dissociation into the electron transfer products.

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Nucleophilic Substitution in Hexachlorocyclopentadiene

S.A.Ismailov

Nucleophilic substitution reactions occurring when hexachlorocyclopentadiene is acted upon by various bases are surveyed and discussed critically. Certain characteristic features of reactions of this type are demonstrated.
The bibliography includes 133 references.

CONTENTS

I. Introduction 41
II. Substitution on treatment with saturated and unsaturated alcohols (monohydric and dihydric), monothiols and dithiols, and monoamines and diamines 41
III. Substitution on treatment with tervalent phosphorus and organometallic compounds 47

I. INTRODUCTION

The "chlorine accumulator",[1] namely hexachlorocyclopentadiene (HCCPD), which is widely used in organic syntheses, has been frequently the subject of review articles[2-5] and a monograph, the first in the periodical literature, devoted to the chemistry of this and related compounds, has been published recently.[6] HCCPD is a unique synthon for perchlorinated skeletal compounds. It was also the first representative of dienes with "reversed electronic character" in relation to the dienophile in the diene synthesis[8,9] and hence permitted the treatment of the mechanism of the Diels–Alder reaction at a still deeper level. By virtue of the ready formation of the aromatic pentachlorocyclopentadienyl anion, HCCPD has become an irreplaceable object for the development of the concept of "X-philic reactions" in organic chemistry.[10]

The diene adducts obtained on its basis are used as fireproofing agents, which make polymers incombustible[11-20] and most of them exhibit pronounced insecticidal,[21-26] fungicidal[27-30] and herbicidal properties.[31-41] Some of these pesticides, such as aldrin, dildrin, etc., are used in the national economy.[42] However, in recent years the range of applications of these compounds has been sharply curtailed and in some countries their use has been prohibited,[43] since they suffer from a significant disadvantage—their natural degradation in nature is slow and it involves the formation of toxic perchlorinated compounds.[44]

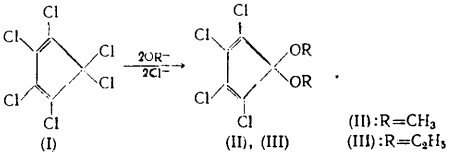
It is believed that one of the possible solutions of this problem is the modification of HCCPD [45] and its diene adducts[46] by substituting some of the chlorine atoms by functional groups. Despite the existing exceptions,[46,48] the substitution of chlorine atoms by alkoxy-groups by the S_N1 mechanism in the HCCPD adducts is usually difficult owing to the high energy of the sp^2-hybridised carbonium anion at the bridgehead of the norbornene skeleton;[49-51] direct substitution also cannot be achieved because of steric hindrance in the attack by the nucleophile from the rear of the bridging carbon atom. Since HCCPD contains two allylic chlorine atoms and four vinyl chlorine atoms and these can be readily exchanged for different anions, the most acceptable and the simplest method of modification involves nucleophilic substitution in the HCCPD itself and not in its adduct. The present review is devoted to such reactions.

Analysis of the literature data demonstrates certain characteristic features of these reactions compared with nucleophilic substitution in other halogenocarbons.

On the other hand, the diene adducts obtained from substituted perchlorocyclopentadienes are of interest, because, by virtue of the presence of the readily hydrolysable ketal group, they are key compounds for the synthesis of useful substances with specified steric structures, which are otherwise difficult to obtain.[52-54]

II. SUBSTITUTION ON TREATMENT WITH SATURATED AND UNSATURATED ALCOHOLS (MONOHYDRIC AND DIHYDRIC), MONOTHIOLS AND DITHIOLS, AND MONOAMINES AND DIAMINES

A number of studies have been devoted to the nucleophilic substitution of chlorine atoms in HCCPD by saturated monoalkoxide anions.[55-59] It was first shown in 1947 [60] that the interaction of HCCPD (I) with KOH in ethanol at room temperature leads to 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene (III) in a high yield. Other 5,5-dialkoxy-1,2,3,4-tetrachlorocyclopentadines can be obtained analogously:[55]



(I) (II), (III) (II): R=CH_3 (III): R=C_2H_5

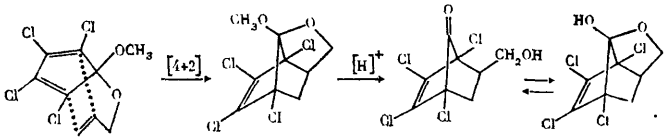
The dienes (II) and (III) are stable compounds which readily enter into the Diels–Alder reaction with various dienophiles, like HCCPD. The stability of these dienes is determined by the presence of the ketal group,[61,62] which ensures the partial shielding of the tetrachlorocyclopentadiene ring and hence hinders the dimerisation process. This is confirmed by the striking tendency of 1,2,3,4-tetrachlorocyclopentadienone,[55] 1,2,3,4-tetrachlorocyclopentadiene,[63] and 1,2,3,4,5-pentachlorocyclopentadiene[64,65] to dimerise via the Diels–Alder reaction.

The high reactivity of HCCPD in nucleophilic substitution has aroused special interest. This compound should apparently be inert with respect to the action of a nucleophile, since direct substitution of the allylic chlorine atoms is difficult owing to steric hindrance to the attack by the nucleophile. Substitution via the ionisation mechanism is impossible, since it requires the formation of the antiaromatic pentadienyl cation, which is destabilised by the overall inductive effect of the five chlorine atoms; this carbonium ion is stable only at low temperature.[66]

Kinetic studies of the interaction between HCCPD and a methanol solution of KOH showed[67] that the reaction is of second order (of first order with respect to HCCPD and the base). Consequently, the rate of reaction is determined by the first bimolecular stage, while a second chlorine atom is substituted in the rapid stage. The authors emphasise that the reaction of HCCPD with an equimolar amount of KOH in

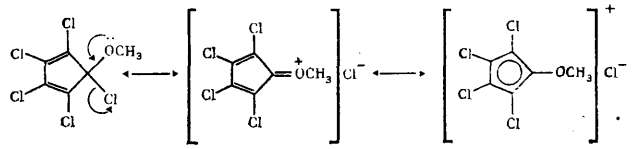
methanol gives rise exclusively to compound (II) both with refluxing and in the cold, approximately 50% of the HCCPD being recovered. It was not possible to detect the intermediate—the monomethoxy-derivative (IV).

However, a study has been recently published[68] in which it was possible to demonstrate indirectly the formation of 1,2,3,4,5-pentachloro-5-monomethoxycyclopentadiene (IV). Treatment of the unpurified diene (II), obtained by the method of McBee et al.,[7] with potassium allylate in allyl alcohol at 50 °C in the course of 4 h led to the isolation of the pure colourless diene (II) and ~3% of compound (VI):



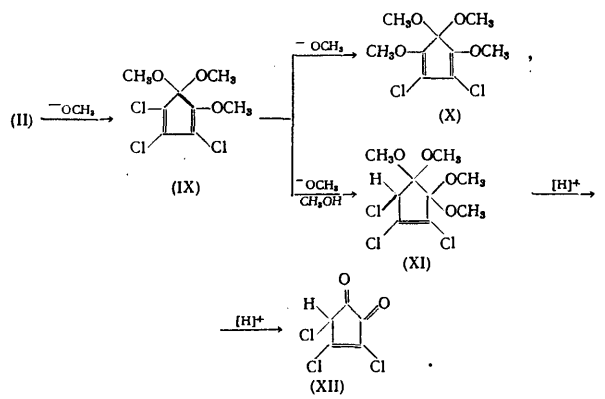
(V) (VI) (VII) (VIII)

The structures of compounds (VI), (VII), and (VIII) obtained were established by spectroscopic methods and by chemical reactions. The intermediate triene (V) can be formed only from the monomethoxy-derivative (IV) when the latter is treated with potassium allylate. The yellow colour of the diene (II) obtained by the method of McBee et al.[67] has been explained by the presence of a small amount of the monomethoxy-derivative (IV) as an admixture, to which the following resonance structures were ascribed:[67]



(IV)

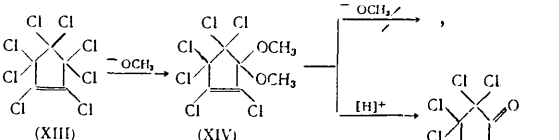
The subsequent reaction of the diene (II) with the methoxide anion is claimed[67] to afford the trimethoxy-compound (IX), which undergoes two simultaneous reactions after brief treatment with the methoxide anion:



(IX) (X) (XI) (XII)

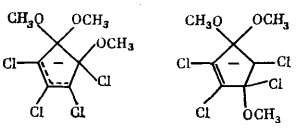
Trichlorotetramethoxycyclopentene (XI), whose structures was inferred from hydrolysis with formation of a compound allegedly identical with the known 3,4,5-trichlorocyclopent-3-ene-1,2-dione (XII),[69] was believed to be the main reaction product under these conditions. However, the position of the OCH_3 group in compounds (IX), (X), (XI), and (XII) was established incorrectly (see below). The tentative diene structure (IX) and (X) of the compound were proved by involving them in the diene condensation with maleic anhydride and also by the IR and UV spectroscopy.

Bimolecular nucleophilic substitution of chlorine in HCCPD could be achieved, in principle, in three positions—at the 1-, 2-, and 5-carbon atoms. Direct substitution of the allylic chlorine atom in the 5-position via the S_N2 mechanism is impossible. The inability of compound (XIV) to react further with the methoxide anion is consistent with this hypothesis:[67]



(XIII) (XIV) (XV)

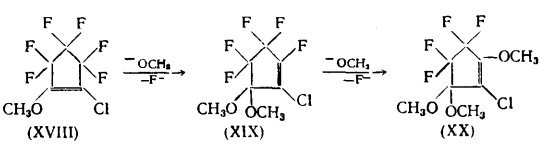
If substitution takes place at one of the two allylic centres in compound (XIII), then the second centre should also react on the reasonable assumption that the dimethoxymethylene group in the product (XIV) does not deactivate the remaining allylic dichloromethylene group. This fact shows that the vinyl position is the centre of attack. The possibility of vinyl attack in these systems follows from the reactivity of the dienes (II) and (IX). The preferred direction of the attack on one of the two centres of the vinyl component of the cyclopentadiene ring has been explained as follows:[67] in reactions of this type, the affinity for nucleophiles characteristic of the substrate undergoing substituion is more important than the polarisability of the nucleofuge. The rate of formation of new bonds depends on the relative stability of the charged intermediate, which is the driving force of the reaction. The increase in the stability of the intermediate anion can be achieved by the charge distribution among several bonds. Hence, in the case of compound (II) there should be two types of vinyl chlorine atoms undergoing substitution and one of two charged intermediates, (XVI) and (XVII), should be formed:



(XVI) (XVII)

The above considerations give preference to the formation of the structure (XVI), but, contrary to expectation, the structure (XVII) is produced, as we shall see below.

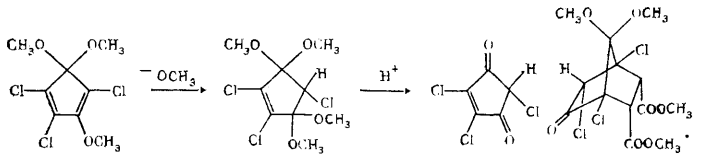
Information about the allylic shift of the double bond and the vinyl attack in these reactions has been obtained[67] with the aid of the reactions of the model compound (XVIII):



(XVIII) (XIX) (XX)

By adding slowly a methanolic solution of alkali to the product (XVIII), compound (XIX) was obtained, whose structure indicates the allylic migration of the double bond on substitution. The subsequent addition of the methoxide ion leads to the product (XX). The formation of compound (XX) indicates vinyl substitution in the 1-position in the cyclopentene ring without involving the chlorine atom, which has

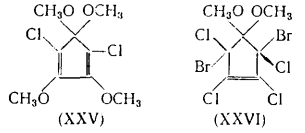
been explained[67] by the relatively high reactivity of the vinyl fluorine atom compared with the vinyl chlorine atom. However, in order to make sure of the reliability of the results, it would be useful to employ the chlorinated analogue of compound (XVIII). This type of substitution in compound (II) should lead to the formation of the structure (XXI) and not (IX). Indeed, when the above reaction was carried out, the authors[70,71] showed that the methoxide anion attacks the carbon atom in the 2-position in the cyclopentadiene ring and compound (XXI) was isolated under these conditions, its structure being established by its conversion into compound (XXII) by treatment with the methoxide anion and acid hydrolysis of this product the corresponding diketone (XXIII):



(XXI) (XXII) (XXIII) (XXIV)

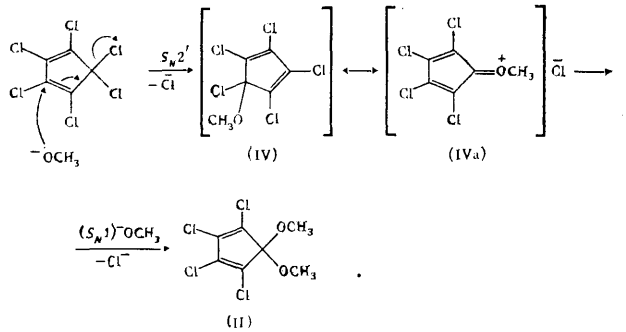
The mistake by McBee et al.[67] was that they attributed the structure of compound (XII) to the ketone (XXIII) obtained. The physicochemical constants of these isomeric ketones are fortuitously identical. The structure of compound (XXI) was demonstrated by diene condensation with dimethyl maleate and the hydrolysis of the product to the corresponding ketone (XXIV). From these data, the structure (XXV) and not (X) can be attributed to the second diene obtained by McBee et al.[67] The structure (XXI) had been attributed to the product as early as 1965 [70] and was then confirmed in 1973;[71] this phenomenon was called the "anomalous effect".

It is noteworthy that the direction of attack by the nucleophile on the vinyl component of the cyclopentadiene ring probably depends on the relative electron density at the carbon atom, i.e. the anion should attack the carbon atom at which the electron density is lowest. Unfortunately, there are no quantitative data concerning this hypothesis for such a system. The vigorous interaction of the diene (II) with electrophilic bromine, leading to the 1,4-adduct (XXVI), may indicate the validity of the above hypothesis.[55]



(XXV) (XXVI)

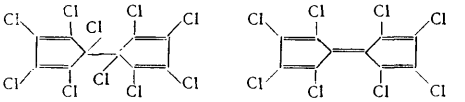
Thus the following mechanism has been put forward[71] based on the kinetic data for the reaction of HCCPD with the methoxide anion[67] and the stereochemical reactions of the products:[70,71]



(IV) (IVa) (II)

As can be seen from this scheme, regardless of the way in which the first chlorine atom in HCPPD undergoes bimolecular substitution, the rate of the second stage of the reaction will be appreciably higher, since the intermediate—pentachloro-5-methoxycyclopentadiene (IV)—undergoes unimolecular exchange of the allylic chlorine via the carbonium ion (IVa), in which the methoxy-group ensures additional resonance stabilisation. On the other hand, the exceptional sensitivity of α-chloro-ethers to bases is well known.[67,69]

It is of interest that compounds (XXVII) and (XXVIII), obtained by the reaction of HCCPD and Cu_2Cl_2, are exceptionally inert with respect to the action of alkoxides,[72,73] which has been explained by steric and resonance effects. These compounds also fail to undergo the diene condensation with dienophiles of different types.

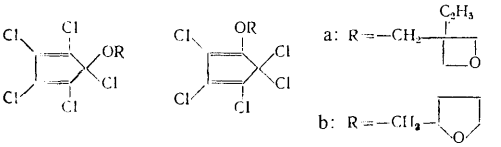


(XXVII) (XXVIII)

The reaction of HCCPD even with more bulky nucleophiles, such as isopropyl, t-butyl,[57] and benzyl alcohols,[74] etc. affords 5,5-disubstituted products. The reactions with phenol[75] and thiophenol[76] give rise to the monosubstituted as well as the disubstituted products.

A study[77] in which the reaction involving the substitution of chlorine in HCCPD by 2-ethylhexoxide was considered and it was shown that it proceeds exclusively with formation of a monosubstituted product—pentachlorocyclopentadienyl 2-ethylhexyl ether—is of considerable interest.

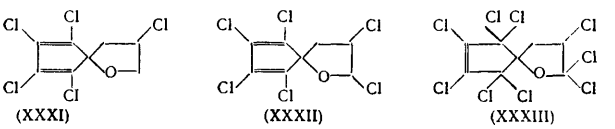
It has also been established[78] that the nucleophilic substitution reaction of HCCPD with two bulky nucleophiles—3-ethyl-3-hydroxymethyloxetan and tetrahydrofurfuryl alcohol—leads simultaneously to two isomeric monosubstituted compounds (XXI) and (XXX) without the formation of disubstituted products:



(XXIX a, b) (XXX a, b)

The authors emphasise that both products interact vigorously with methanol in the presence of acid catalysts and that R is then substituted by CH_3. However, the reaction mechanism is not described. The absence of *gem*-disubstituted products in this reaction has been explained by steric factors generated by the nucleophiles themselves. The structures of the compounds obtained were established by the analysis of their IR spectra and of the Diels–Alder adducts obtained with various dienophiles. The formation of the isomer (XXX) is probably associated with the 1,5-migration of the chlorine atom in the cyclopentadiene ring.

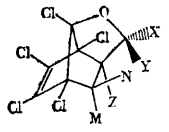
The nucleophilic substitution of a chlorine atom in HCCPD by unsaturated anions has its characteristic features. It has been claimed[79] that, when the allylate anion reacts with HCCPD, the monosubstituted adduct (XXXI) is formed.



(XXXI) (XXXII) (XXXIII)

A patent[80] describes a study of the chlorination reaction of this compound, which allegedly yielded compounds (XXXII) and (XXXIII), but the structure (XXXI) attributed to the initial compound is incorrect.

Sometime later, an analogous reaction was carried out with monomethyl-substituted allyl alcohols and it was discovered that it takes place readily at 25–30 °C in aprotic solvents with formation of the oxatricyclononene skeleton: [81]

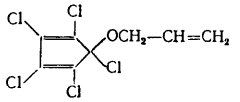


(XXXIV)

where X, Y, Z, M, and N are various alkyl and aromatic groups.

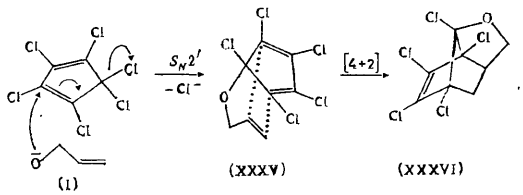
It is noteworthy that the author[81] does not reject the formation of compound (XXXI) in the case of allyl alcohols; an attempt was made to account for the cyclisation reaction in the formation of compound (XXXIV) by the electronic and structural effects generated by the alkyl or aryl substituents.

In 1969 the reaction with allyl alcohol was repeated[82] under fairly severe conditions (100–150 °C) and the structure (XXXV) was attributed to the product thus obtained:



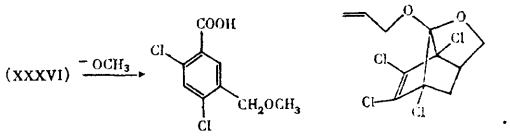
(XXXV)

However, spectroscopic data and data based on chemical reactions are not quoted to prove the structure of the final products. It was shown later[83] that the compound obtained under these conditions does not react with maleic anhydride and that there are no absorption bands of the diene chromophore in its UV spectrum (in methanol). It was found that the position of the absorption maximum and its intensity (λ_{max} = 238 nm, ε = 2800) are identical with those calculated for the pentachlorocyclopentene structure. On the other hand, the IR spectrum of this compound contains one narrow absorption band at 1620 cm^{-1}, which is characteristic of the ClC=CCl fragment instead of the two bands which are usual for structures of type (XXXV). The structure of the compound obtained was finally established by analysing its ^1H NMR spectrum using nuclear double resonance. The ^1H NMR spectrum reveals the absence of allylic protons and is fully consistent with the structure (XXXVI). Compound (XXXV) is evidently a precursor in the formation of the final product (XXXVI) via the mechanism



(I) (XXXV) (XXXVI)

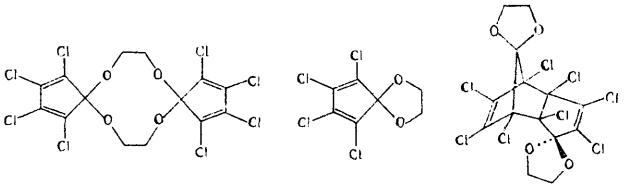
Compound (XXXVI) is formed as a result of the intramolecular [4 + 2]cycloaddition of the intermediate unstable triene (XXXV). The subsequent reaction involving substitution by anions via the S_N1 mechanism in the adduct (XXXV) was not observed under these conditions. However, on refluxing in a methanolic solution of alkali, the product (XXXVI) undergoes a skeletal rearrangement with formation of 4,6-dichloro-3-methoxymethylbenzoic acid (XXXVII), whose structure was determined by spectroscopic and chemical methods: [84]



(XXXVII) (XXXVIII)

The corresponding data confirming the structure (XXXVI) were also obtained almost simultaneously by Jung and Light; [85] in addition, they obtained 15% of the disubstituted product (XXXVIII).

Nucleophilic substitution in HCCPD by various diols has been investigated comprehensively. [86–93] Using ethylene glycolate as the nucleophile, the crystalline compound (m.p. 279 °C), to which the structure (XXXIX) was attributed, had been obtained even earlier: [55]

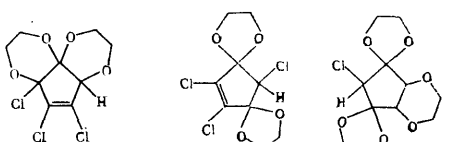


(XXXIX) (XL) (XLI)

It was latter established[87] that, when this reaction is carried out under fairly mild conditions (15 °C) and in the presence of a sixfold excess of ethylene glycol, the formation of low-melting crystals (m.p. 65–66 °C) is observed; the structure of the compound (XL) obtained was determined mainly chemically—by involving it in the diene condensation with various dienophiles. Thus the product was a monomer—a spirodiene.

This reaction was investigated in even greater detail by Chang; [86] three crystalline compounds were then isolated (m.p. 107–108.5°, 79.5–80°, and 64.5–65.5 °C). The substance with m.p. 64.5–65.5 °C, which is 1,2,3,4-tetrachloro-6,9-dioxaspiro[4,4]-nona-1,3-diene (XL), can be obtained in 90% yield from one mole of HCCPD, 2.1 moles of KOH, and 8 moles of ethylene glycol. On heating (2 h, ~100 °C) or on storage in solutions for a fairly long time, compound (XL) dimerises to the product (XLI) (m.p. 279 °C) and not the product (XXXIX). The structure (XLI) was established chemically (this compound is inert to the action of dienophiles) and spectroscopically. The high tendency of the diene (XL) to dimerise, in contrast to the diene (II), has been explained by the steric influence of the ketal group. However, the author did not establish the structures of the other two compounds which he obtained (with m.p. 107–108.5° and 79.5 to 80 °C).

Subsequently, this reaction was investigated[70] at relatively high temperatures (55–60 °C) and mainly five compounds were then obtained: (XL), (XLI), (XLII), (XLIII), and (XLIV).

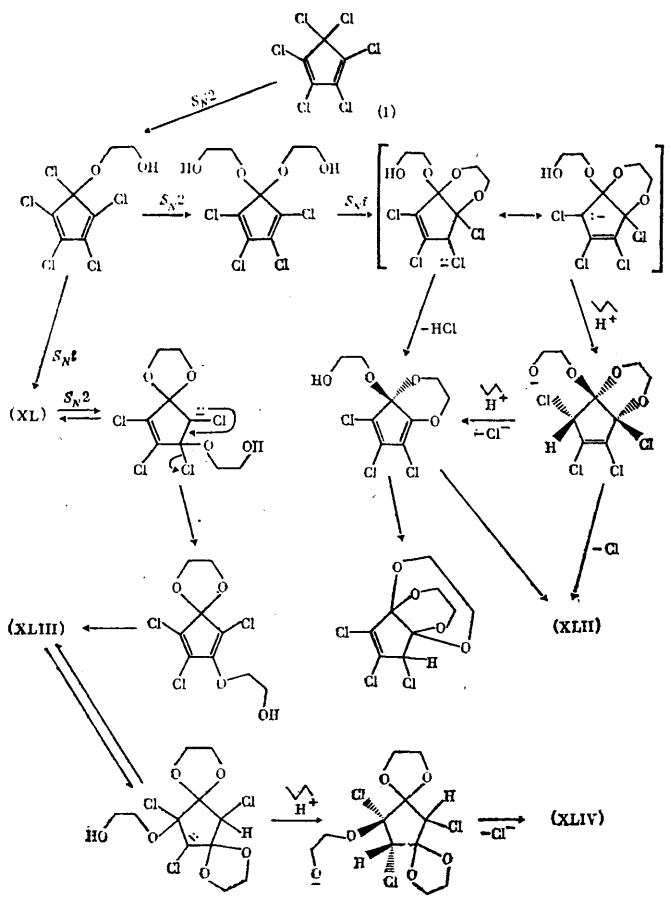


(XLII) (XLIII) (XLIV)

In the presence of an excess of the glycol and alkali and under more severe conditions (50–120 °C) the product (XLII) is formed. (On raising the reaction temperature to

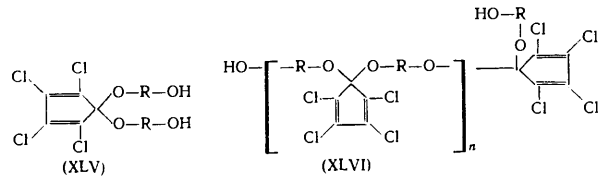
140 °C, the formation of compound (XLIV) is observed.[92] The proposed reaction mechanism[70] is indicated in Scheme 1.

Scheme 1



As can be seen from this scheme, the author attempts to explain the initial attack by the nucleophile from the standpoint of the S_N2 mechanism, but this is impossible, as noted above. On the other hand, the monoalkoxy-intermediate formed should also be converted into the dialkoxy-compound via the S_N1 mechanism and not the S_N2 mechanism.[67,71]

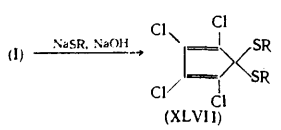
The interaction of HCCPD with polyhydric alcohols containing ≥2 hydroxy-groups, compounds with non-neighbouring carbon atoms, leads to the formation of 1,2,3,4-tetrachloro-5,5-di(hydroxyalkoxy)cyclopentadienes (XLV) and the polyketals (XLVI):[90]



(XLV) (XLVI)

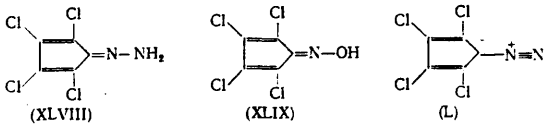
The ratio of the products obtained depends on the stoichiometry of the initial components taken for the reaction.

The reactions between HCCPD and various thiols in alcohol solution, leading to 5,5-thioketals (XLVII), proceed analogously to the reactions of HCCPD with alcohols:[57,94]



(XLVII)

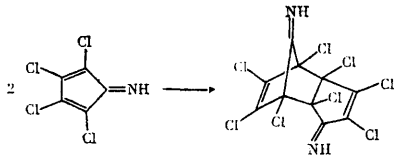
HCCPD reacts actively with hydrazine and hydroxylamine, which results in the formation of tetrachlorocyclopentadienone hydrazone (XLVIII) and oxime (XLIX):[95-98]



(XLVIII) (XLIX) (L)

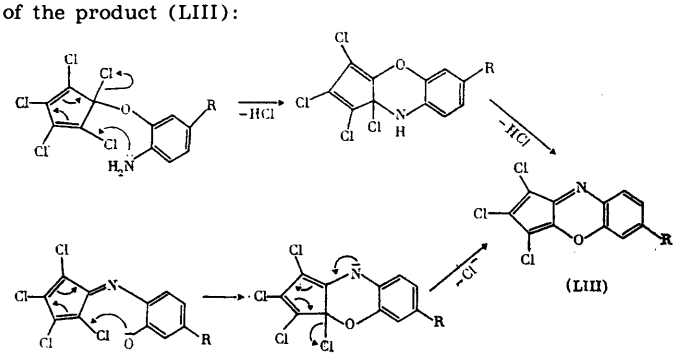
Dehydrogenation of the product (XLVIII) leads to the formation of tetrachlorodiazocyclopentadiene (L) in a high yield. In contrast to 1,2,3,4-tetrachlorocyclopentadienone, the above compounds are stable at room temperature.

It is of interest that the substitution product (LI), obtained by the reaction of HCCPD with ammonia at low temperatures (~−70 °C), is unstable and dimerises at the instant of formation to form the bisimine (LII):[99-100]



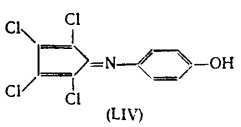
(LI) (LII)

The interaction of HCCPD with *o*-aminphenols in the presence of C_2H_5ONa yields[101] cyclopentabenzoxazines (LIII). The authors quote two alternative mechanisms of formation of the product (LIII):



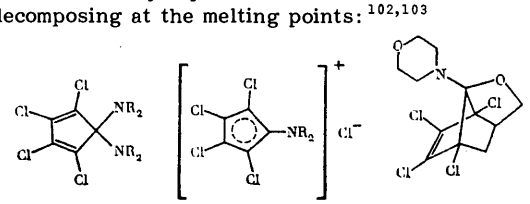
(LIII)

Which of the two nucleophilic centres (NH_2 or OH) is the first to be attacked has been demonstrated by using *p*-aminophenol as the nucleophile, which affords a single product—*p*-hydroxyazafulvene (LIV), which indicates the dominant role of the NH_2 group compared with the hydroxyl in this reaction:



(LIV)

When secondary amines such as morpholine, piperidine, and dimethylamine are used as the nucleophiles, 5,5-disubstituted tetrachlorocyclopentadienes (LV) are formed as a rule, decomposing at the melting points:[102,103]

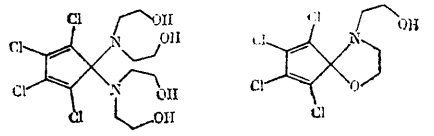


(LV) (LVa) (LVI)

The monosubstituted product (LVa) was not isolated, which the authors explain by its instability when acted upon by bases.

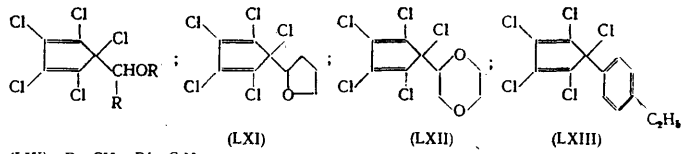
It is curious that treatment of compound (LV) with allyl alcohol for 4 weeks (25 °C) entails the replacement of one morpholino-group by the allylate anion with formation of the oxatricyclononene structure (LVI).

The interaction of diethanolamine with HCCPD led to the spiro-compound (LVIII) and not to the usual substitution product (LVII):[104,105]



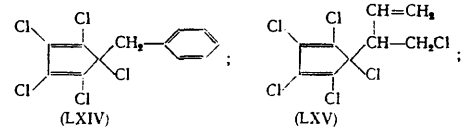
(LVII) (LVIII)

The HCCPD derivatives (LIX)–(LXIX) monosubstituted by functional-groups in the 5-position, synthesised by photo-initiated radical reactions,[106,107] undergo nucleophilic substitution on reaction with two typical nucleophiles: the methoxide anion and morpholine;[45] it was shown that the reaction proceeds in two stages with formation of 5,5-disubstituted products:

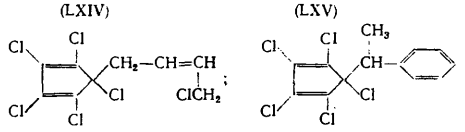


(LXI) (LXII) (LXIII)

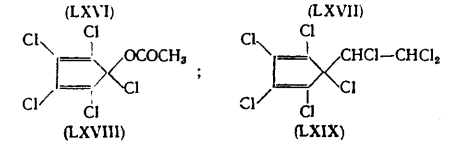
(LIX): R=CH_3, R'=C_2H_5
(LX): R=CH_2Cl, R'=C_4H_9



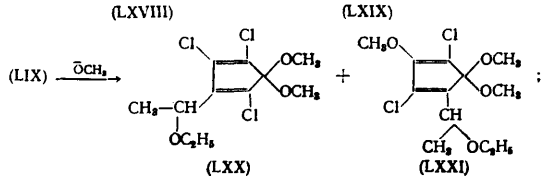
(LXIV) (LXV)



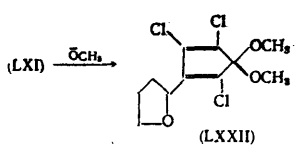
(LXVI) (LXVII)



(LXVIII) (LXIX)



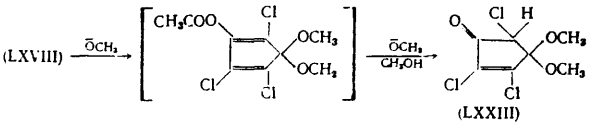
(LXX) (LXXI)



(LXXII)

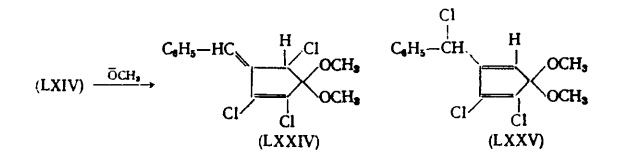
After prolonged heating, the authors were able to isolate the trimethoxy-derivative (LXXI).

The 5-acetoxy-derivative (LXVIII) readily reacts with the methoxide anion, which affords a high yield of the ketone (LXXIII):[45]



(LXXIII)

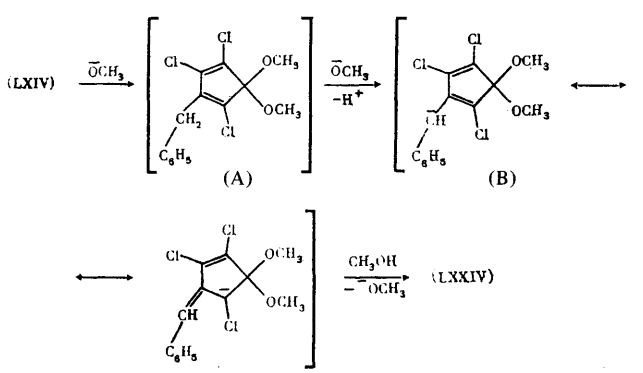
The authors emphasise that the interaction of compounds (LXIV) and (LXVII) with the alkoxide proceeds in a more complex manner and that the rearranged products (LXXIV) and (LXXVII) are then formed in satisfactory yields:



(LXXIV) (LXXV) (LXXVI) (LXXVII)

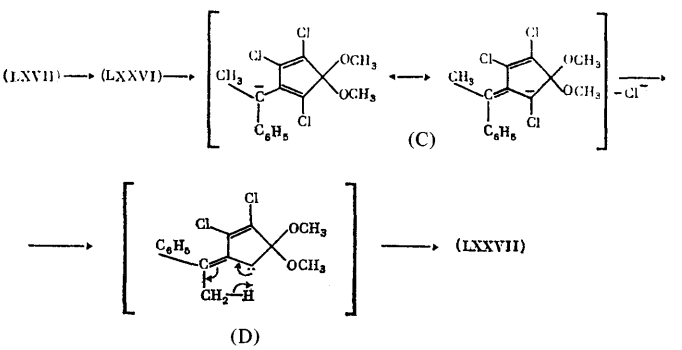
Compound (LXXVI) is fully converted during the reaction into the product (LXXVII). It has been established on the basis of spectroscopic data that the structure (LXXIV) is more probable than the structure (LXXV).

Consequently, the reactions of the benzyl compounds proceed in an unusual manner and involve three stages—methoxylation, dehydrochlorination, and hydrogen transfer from the substituent to the cyclopentadiene ring:



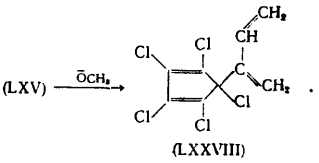
(A) (B) (LXXIV)

Compound (LXXVII) can also be obtained via the above pathway, but the subsequent conversion of the anion (C) into the carbene (D) and the 1,4-sigmatropic shift in the latter lead to the product (LXXVII):



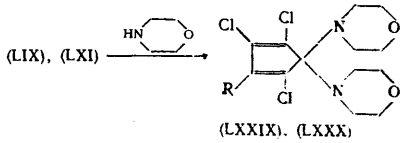
(C) (D)

Treatment of compound (LXV) with an equivalent amount of the alkoxide results in an almost quantitative formation of the bisdiene (LXXVIII):[45]



(LXXVIII)

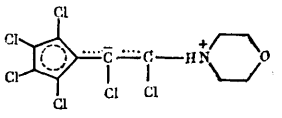
Compounds (LIX) and (LXI) react readily with morpholine, forming the 5,5-disubstituted products (LXXIX) and (LXXX):



(LXXIX), (LXXX)

(LXXIX): R=CH(CH$_3$)OC$_2$H$_5$; (LXXX): R=

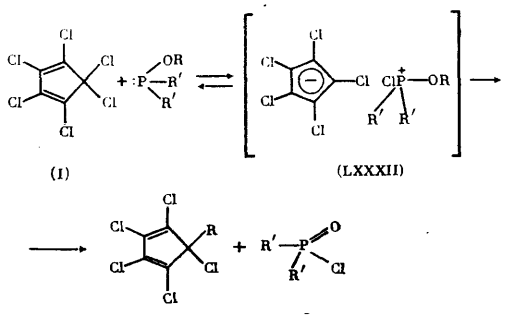
The reaction between the diene (LXIX) and morpholine proceeds differently and results in the formation of a dark-red product having the overall formula $C_{11}H_9Cl_6NO$. The structural formula (LXXXI) was attributed to it from spectroscopic data and physical properties:



(LXXXI)

III. SUBSTITUTION ON TREATMENT WITH TERVALENT PHOSPHORUS AND ORGANOMETALLIC COMPOUNDS

The high tendency of HCCPD to form the stable aromatic pentachlorocyclopentadienyl anion on interaction with tervalent phosphorus and organometallic compounds has led to a new effective way of obtaining halogenocyclopentadienes with functional-group substituents[108–110] and has stimulated the development of the field of halogenophilic reactions.[10] According to the mechanism proposed by Mark,[111] the above reaction is a two-stage process; the allylic chlorine is abstracted by the nucleophile in the first stage with formation of the pentachlorocyclopentadienyl anion (LXXXII), while in the second stage the latter is alkylated with formation of 5-alkylpentachlorocyclopentadiene (LXXXIII):

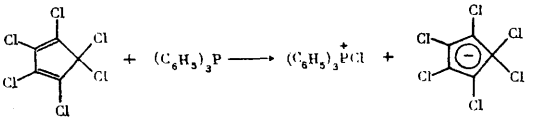


(I) (LXXXII)

(LXXXIII)

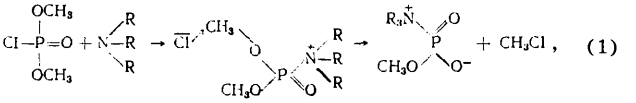
Repeated alkylation of compound (LXXXIII) gives rise to a mixture of three isomers: 5,5-, 1,5-, and 2,5-dialkyltetrachlorocyclopentadienes. Alkylation of HCCPD via the above scheme does not proceed in accordance with the S_N2 mechanism, in contrast to the Arbuzov rearrangement, which has been confirmed by the reactions of sterically hindered phosphites (t-butyl dimethyl phosphite, t-butyl diethyl phosphite) with HCCPD, which lead to the formation of 5-monosubstituted pentachlorocyclopentadienes.

The ^{31}P NMR signal of the chlorotriphenylphosphonium cation (LXXXIV) has been detected on interaction of HCCPD with triphenylphosphine (at −80 °C), which indicates the simultaneous formation of the anion (LXXXII):[112]

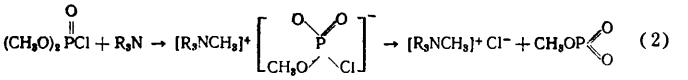


(LXXXIV) (LXXXII)

The use of trimethyl phosphite as the nucleophile led to charring of the reaction mixture as a consequence of the formation of the very reactive intermediate $(CH_3O)_2POCl$ during the reaction. In order to eliminate this difficulty, the equivalent amount of a tertiary amine, which decomposes the undesired product $(CH_3O)_2POCl$ via the mechanisms (1) or (2),[113] was added to the reaction mixture:



(1)

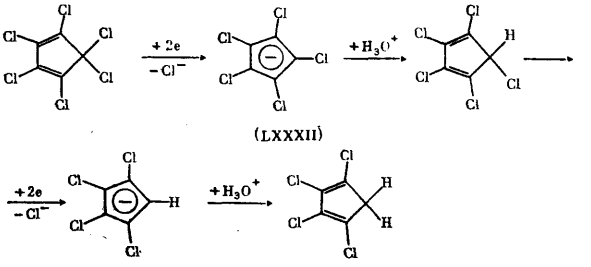


(2)

If the phosphorus atom is the centre of nucleophilic attack, then the reaction proceeds via the mechanism (1).

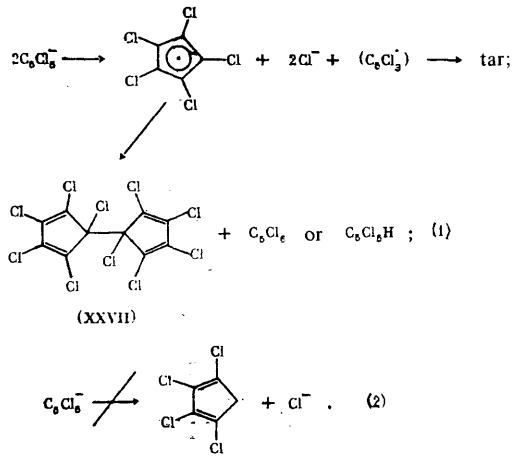
Tri-t-butyl phosphite exhibits a high reactivity in its reaction with HCCPD.[110] The high reactivity of this nucleophile can be accounted for by the high inductive effect of the t-butyl group compared with the normal alkyl groups and also by its large bulk, which increases the O–P–O angle and results in the approach of the hybridisation of the valence electrons of phosphorus to the sp^3 type. This facilitates the transition to the tetracoordinate state.

The formation of the anion (LXXXII) has also been demonstrated by the electrochemical reduction of HCCPD at a dropping mercury electrode in unbuffered and acid aqueous ethanol solutions:[114,115]



(LXXXII)

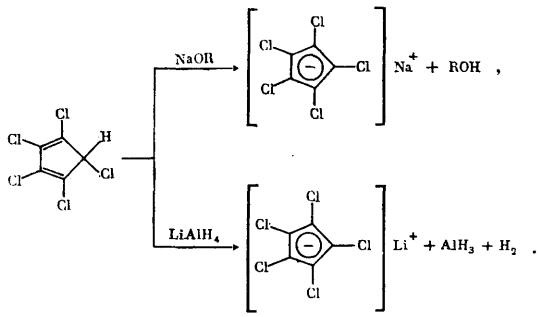
It is noteworthy that the basicity[114] and nucleophilicity[116–118] of the anion (LXXXII) are low, but the anion is rapidly oxidised with formation of the pentachlorocyclopentadienyl radical, owing to the overlap of the occupied π orbitals of the cyclopentadiene ring with the $3p_y$ orbitals of chlorine and this destabilises the π orbitals:



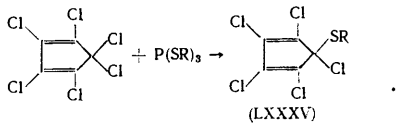
(XXVII)

The isolation of bispentachlorocyclopentadienyl (XXVII) serves as confirmation of the proposed mechanism (1).[116]

The anion (LXXXII) is also readily generated from pentachlorocyclopentadiene by reaction with strong bases:[65,116,118]

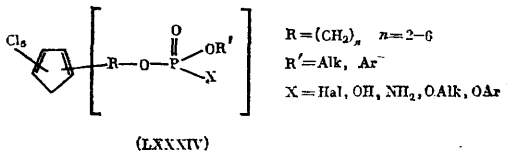


In contrast to the reaction of trialkyl phosphites with HCCPD, the interaction of the latter with trialkyl phosphorothioites leads to the formation of 1,2,3,4,5-pentachlorocyclopentadienyl sulphide (LXXXV), which exhibits a high biological activity:[119,120]



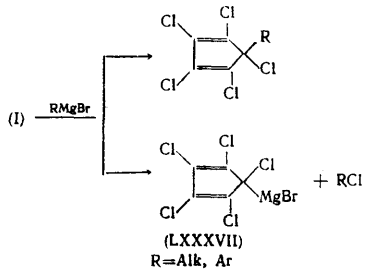
(LXXXV)

In contrast to acyclic phosphites, cyclic phosphites having the general formula OROPOR′, give rise on reaction with HCCPD, to pentachlorocyclopentadienyl phosphates (LXXXVI)[121,122] possessing insecticidal and herbicidal activities:



(LXXXIV)

HCCPD interacts vigorously with Grignard reagents, which results in the formation of monosubstituted products and other secondary compounds:[123,124]



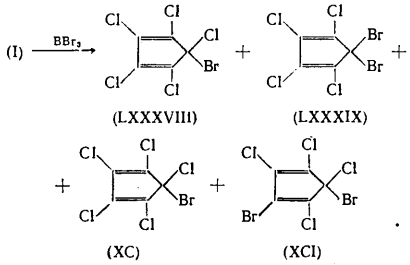
(LXXXVII)
R=Alk, Ar

The authors were unable to obtain a Grignard reagent from HCCPD by the direct interaction of the latter with magnesium owing to the marked charring of the reaction mixture. It was therefore necessary to obtain initially the Grignard reagent of a halogenohydrocarbon and, by the reaction of the latter with HCCPD, to synthesise the desired product (LXXXVII). It was established that one chlorine atom is substituted by MgBr in this reaction, since only 1,2,3,4,5-pentachlorocyclopentadiene and a small amount of its dimer are formed on dilution of the reaction mixture with water. In addition two further compounds were isolated from the reaction mixture—bispentachlorocyclopentadienyl and a hydrocarbon. The interaction of HCCPD with RMgBr and subsequent mixing with solutions of halogenohydrocarbons in ether lead to 5,5-disubstituted derivatives of HCCPD.[123]

The chlorophilic reaction strikingly manifests the extensive synthetic possibilities for the preparation of new HCCPD derivatives with functional-group substituents in the synthesis of mixed polyhalogenocyclopentadienes.[125–132]

During recent years, much attention has been devoted to the synthesis of polyhalogenocyclopentadienes in connection with the vigorous development of ecological chemistry and the chemistry of skeletal compounds with functional-group substituents.[7,125]

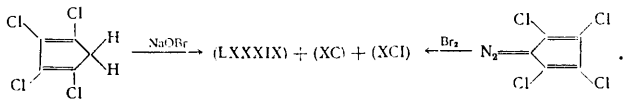
In the temperature range 160–170 °C, HCCPD reacts with PBr_3 to form 5-bromo-1,2,3,4,5-pentachlorocyclopentadiene.[127] In the presence of a catalytic amount of $AlBr_3$, the above reaction with PBr_3 leads to the successive substitution of chlorine atoms by bromine.[128,129] However, the question of the isomerism of the mixed polyhalogenocyclopentadienes obtained was not considered in these investigations and the authors unambiguously attributed structures with bromine atoms at C(5) to the compounds synthesised. ^{13}C NMR has been used to demonstrate the structures.[125] It was established reliably on the basis of the spectroscopic data that the reaction products are 5-bromo-1,2,3,4,5-pentachlorocyclopentadiene (LXXXVIII), 5,5-dibromotetrachlorocyclopentadiene (LXXXIX), 1,5-dibromotetrachlorocyclopentadiene (XC), 2,5-dibromotetrachlorocyclopentadiene (XCI), and a small amount of an extensive bromination product.



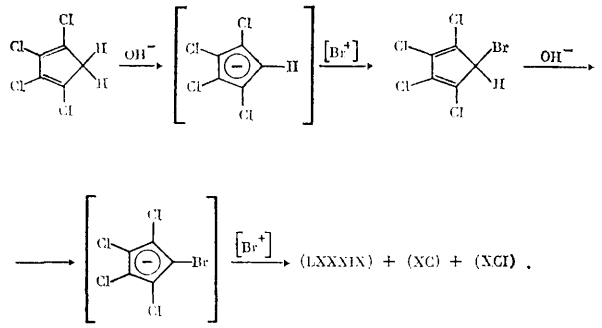
(LXXXVIII) (LXXXIX)

(XC) (XCI)

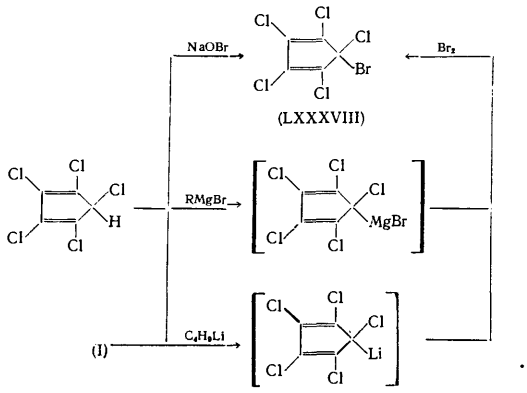
Compounds (LXXXIX), (XC), and (XCI) have been obtained by brominating tetrachlorocyclopentadiene with sodium hypobromite or by the interaction of tetrachlorodiazocyclopentadiene with bromine:[125]



This yields a mixture of three isomers in approximately equal proportions. The simultaneous formation of three dibromide isomers on bromination of tetrachlorocyclopentadiene was explained by the authors[125] with the aid of the following scheme:

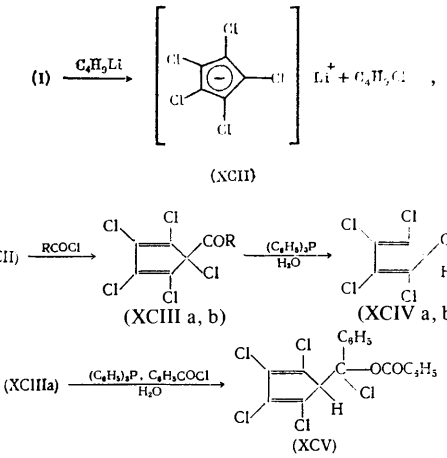


The absence of monobromides with vinyl hydrogen atom from the reaction products indicates the regioselective attack by the electrophilic bromine on the 5-position in the anion (E). However, attack on the anion (F) by the electrophile can also take place non-regioselectively, which in fact results in the formation of three isomers. The monobromide (LXXXVIII) has been obtained by the reaction of pentachlorocyclopentadiene with NaOBr and also by the reaction of pentachlorocyclopentadienylmagnesium bromide or pentachlorocyclopentadienyl-lithium with bromine:[125]



Contrary to the data of Williamson et al.,[130] Zaichikova et al.[125] established, on the basis of chemical reactions and with the aid of ^{13}C NMR, that the bromine atom does not migrate in the cyclopentadiene ring in the monobromide (LXXXVIII) on heating and under the conditions of this diene synthesis.

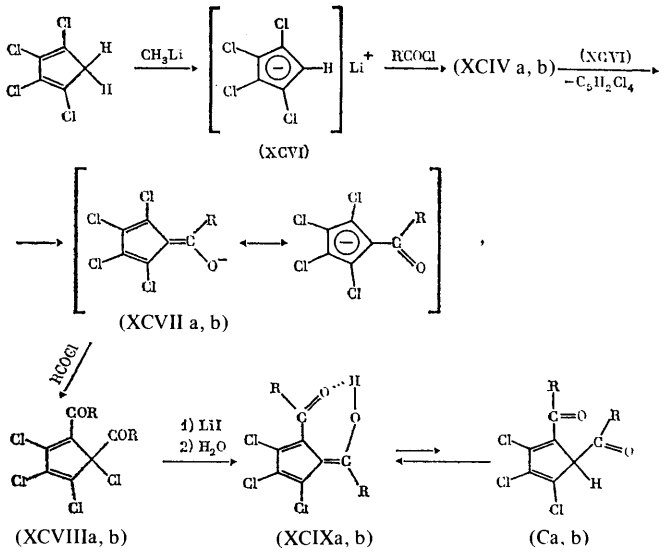
Pentachloro- and tetrachloro-cyclopentadienyl-lithium are widely used in the synthesis of HCCPD derivatives monosubstituted by functional groups.[65,126,133] A new method of synthesis of compound (XLII) has been developed and a number of syntheses based on it have been carried out.[126] In contrast to the known procedures for synthesising compound (XCII) with the aid of lithium amalgam and $LiAlH_4$,[118] it was synthesised from HCCPD and butyl-lithium in pentane at −70 °C and was immediately made to react with strong electrophiles—carboxylic acid chlorides,[126] which results in the formation of unstable 5-acylpentachlorocyclopentadienes (XCIIIa, b):



These ketones (XCIIIa, b) are used in synthesis without additional purification at the instant of their formation, as shown in the scheme.

An unexpected result has been obtained[126] in the reduction of the ketone (XCIIIa) by triphenylphosphine in the presence of an excess of benzoyl chloride. It was established from spectroscopic data that, together with the formation of compound (XCIVa), its enolic form is acylated with the intermediate formation of tetrachlorophenylbenzoyloxyfuvene and the addition to the latter of hydrogen chloride. The structure of compound (XCV) was confirmed by its specific synthesis.

The acetylation of tetrachlorocyclopentadienyl-lithium (XCVI) with acetyl chloride at −50 °C led to the stable crystalline product (XCIXb) whose structure was determined by spectroscopic methods; for example, the signal due to the chelate proton in the ^1H NMR spectrum is in the region of $\delta = 16.10$ p.p.m.



Thus the existing experimental data on nucleophilic substitution in HCCPD demonstrate that this structurally simple compound has interesting chemical properties and reveal the following features of reactions of this type.

Nucleophilic substitution of the chlorine atoms in HCCPD by alkoxides, thiolates, and amines proceeds in two stages: initially the anion attacks the 2-position in HCCPD via the S_N2' mechanism and then the allylic chlorine atom (in the 5-position) is abstracted via the S_N1 mechanism and the final reaction products are 5,5-disubstituted 1,2,3,4-tetrachlorocyclopentadienes.

Substitution by treatment with alkoxides obtained from allyl alcohol and its derivatives proceeds anomalously with formation of 5-monosubstituted products.

Substitution by treatment with tervalent phosphorus and organometallic compounds takes place with formation of the aromatic pentachlorocyclopentadienyl anion, whose alkylation affords 5-alkyl-1,2,3,4,5-pentachlorocyclopentadiene.

However, together with the above findings, there exist also unsolved problems in this field, in particular there are no data concerning the carbanionic (Ad_N type) addition—elimination mechanism, which may compete with the mechanism of the S_N2' type in the reactions of HCCPD with alkoxides (the formation of 1,3,4-trichloro-5,5-difluoro-2-methoxycyclopentadiene on interaction of 1,2,3,4-tetrachloro-5,5,difluorocyclopentadiene, a derivative of a HCCPD homologue, with the methoxide anion can be readily explained with the aid of the Ad_N mechanism[65,71]); the formation of only monosubstituted products in the reaction of HCCPD with certain saturated alcohols is unexpected;[77,78] there have been no quantum-chemical calculations for HCCPD and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, with the aid of which it might be possible to predict the regioselectivity of the reactions, etc.

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Reactions Involving the Addition of Dithio-acids to Unsaturated Compounds

V.N.Drozd, M.L.Petrov, N.Ya.Kuz'mina, and A.S.Vyazgin

Data on the reactions involving the addition of dithiocarboxylic, dithiocarbamic, and other heterosubstituted dithio-acids to compounds with a multiple bond are surveyed. It is shown that the character of the addition depends on the nature of the dithio-acid: dithiocarbamic and xanthic acids add via an ionic mechanism, while for dithiocarboxylic acids there is a possibility also of radical addition as well as cycloaddition together with the ionic addition.
The bibliography includes 126 references.

CONTENTS

I. Introduction 52
II. Dithiocarbamic and xanthic acids 52
III. Dithiocarboxylic acids 56

I. INTRODUCTION

In contrast to the reactions involving the addition of carboxylic acids to multiple bonds, which have been investigated in detail, those of the sulphur analogues (dithio-acids) have attracted the attention of investigators relatively recently. The interest in these reactions is associated both with the active development of the chemistry of organosulphur compounds and with the practical application of dithio-acid esters—the products of the interaction of unsaturated compounds and dithio-acids.

Divinyl sulphide and its derivatives have been obtained by reactions of dithio-acid salts.[1-4] The vinyl esters of various dithio-acids have found applications in the synthesis of polymeric materials.[5-9] The products of the interaction of dithio-acids with unsaturated compounds have a fairly broad spectrum of biological activity. Thus dithiocarbamic acid esters exhibit insecticidal, acaricidal, nematocidal, and fungicidal activities.[10-13] A wide variety of heterocyclic sulphur derivatives have been obtained from the products of the interaction of dithio-acids with unsaturated compounds. For example, one may note the synthesis of sulphur analogues of pyrimidine derivatives which form part of the composition of nucleic acids—uracil and thymine,[14] as well as the synthesis of derivatives of tetrathiafulvalene, which are used to obtain "organic metals"—radical-ion salts with conducting properties.[15]

In connection with the undoubted practical value of dithio-acid esters, their properties and the methods of their synthesis have been considered in fair detail in a series of books, monographs, and reviews.[1-4,16-19] However, the reactions involving the addition of dithio-acid to unsaturated compounds have not been described in these publications.

The present review is devoted to the consideration of the characteristic features of reactions involving the addition of dithio-acids to the multiple bonds of a wide variety of unsaturated compounds.

II. DITHIOCARBAMIC AND XANTHIC ACIDS

1. The Addition of Dithiocarbamic and Xanthic Acids to Double Bonds

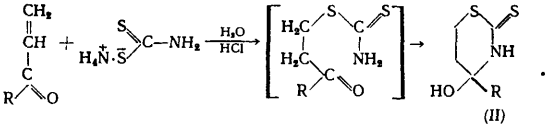
The first reactions of dithio-acids with unsaturated compounds were carried out in relation to the interaction of unsubstituted and *N*-monosubstituted dithiocarbamic acid with alkenes activated by electron-accepting substituents. The regioselectivity of the reaction and the fact that the reactions are carried out in polar solvents (water, alcohol) permit the claim that all cases involve the ionic addition of dithiocarbamic acid with formation of dithio-esters (I) in high yields (60–90%):[20-26]

$$R^1NHCS_2H + R^2R^3C{=}R^4Z \rightarrow R^1NHC(S)SCR^2R^3CHR^4Z \quad (I)$$

$R^1 = H, Alk; R^2, R^4 = H, Alk; R^3 = H, Alk, Ar, CCl_3;$
$Z = CHO, CONAlk_2, COAlk, CO_2Alk, CN.$

The exclusively ionic character of the addition can probably be accounted for by the fact that the unsubstituted and *N*-monosubstituted dithiocarbamic acids, generated by treating ammonium salts with HCl, can behave as the inner salts $R\overset{+}{N}H_2C(S)S^-$ under the reaction conditions.

The dithio-esters (I), obtained by condensing dithiocarbamic or *N*-alkyldithiocarbamic acids with αβ-ethylenic carbonyl compounds, have been converted by intramolecular cyclisation into the corresponding 1,3-thiazines (II),[21,23,24] sometimes without isolating compounds (I):[22]



(II)

In the reactions of dithiocarbamic acids with substituted divinyl ketones, the attack is directed to the less substituted double bond:[26]

$$Me_2C{=}CHCOCH{=}CH_2 \xrightarrow[-5^\circ C, HCl]{RR^1NCS_2^-N^+H_4(Na^+)} Me_2C{=}CHCOCH_2CH_2SC(S)NR^1R;$$
$R = H, Alk, R^1 = Alk, Ar, PhCH_2.$

The reactions of salts of dithiocarbamic acids with alkenes, activated by electron-accepting substituents, also lead to the dithio-esters (I):[13,27-35]

$$R^1R^2NCS_2^-Kat^+ + R^3R^4C{=}CR^5Z \xrightarrow{H_2O} R^1R^2NC(S)SCR^3R^4CHR^5Z \quad (I)$$

$R^1, R^2 = H, Alk, (CH_2)_n; R^3, R^4, R^5 = H, Me, Ph; Z = COAlk,$
$CO_2Alk, CONH_2, CN, NO_2, SO_2Alk; Kat = K, Na, NH_4, AlkNH_3, Alk_2NH_2, Alk_3NH.$

It has been noted in a number of studies[29,30] that, together with the dithio-esters (I), the reaction mixture contains considerable amounts of the sulphides $(ZCHRCHR)_2S$ (III), the sulphide becoming the main product in the presence of an

excess of the base. A possible mechanism of the formation of these compounds has been put forward:

$$RNHCS_2^-Na^+ + H_2C=CHCN \xrightarrow{H_2O} (I) + NaOH,$$
$$(I) \xrightarrow{OH^-} RN=C=S + HSCH_2CH_2CN;$$
$$HSCH_2CH_2CN + H_2C=CHCN \rightarrow (NCCH_2CH)_2S.$$

However, the possibility that the sulphide ion is generated in the rearrangement of the dithiocarbamate anion to isothiocyanate under the influence of the base is not ruled out:

$$RNHCS_2^- \rightleftarrows RN=C(S^-)SH \xrightarrow{OH^-} RN=C=S + S^{2-} + H_2O;$$
$$S^{2-} + 2H_2C=CHCN \xrightarrow{H_2O} (NCCH_2CH_2)_2S.$$

In order to increase the yield of compound (I), it has been suggested that the reaction be carried out in the presence of acetic acid and with cooling (at 0 °C).[30]

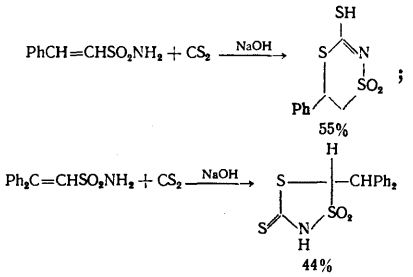
Reactions of dithiocarbamic salts with activated alkenes are reversible and are accompanied by the isomerisation of the alkenes:[10,31,34,36-38] in the reaction of triethylammonium *NN*-diethyldithiocarbamate with dimethyl fumarate, the equilibrium is attained when 82% of the reaction product (I) has accumulated in the mixture.[39]

The reaction of perfluoropropene with sodium *NN*-dialkyldithiocarbamate in an effectively solvating solvent [dimethylformamide (DMF)] affords, together with the expected product (I) of the addition of the dithiocarbamate anion to the double bond, also the product (IV) of the substitution of the fluorine atom at the double bond by the dithiocarbamate group:[40]

$$CF_3CF=CF_2 + R_2NCS_2^-Na^+ \rightarrow \underset{(I)}{CF_3CFHCF_2SC(S)NR_2} + \underset{(IV)}{CF_3CF=CFSC(S)NR_2}.$$

However, it has been shown[40] that a mixture of the (*Z*)- and (*E*)-isomers of compound (IV) is formed when hydrogen fluoride is eliminated from the dithio-ester (I) under the reaction conditions.

The reaction, described by Hasegawa et al.,[41,42] can be classified as an example of intramolecular nucleophilic addition of the dithiocarbamate anion to the double bond:



In the presence of electron-donating substituents in the *para*-position in the benzene ring, the yields increase to 95%.

The reactions of organyldithiocarbamic acids, formed from carbon disulphide and a secondary amine, with alkyl vinyl ethers and sulphides has been investigated recently; in the general case, the reaction proceeds as electrophilic addition, leading to 1-alkoxy- and 1-alkylthio-1-(organyldithiocarbamoyl)ethanes in yields ranging from 77% to quantitative:[43,44]

$$2R^1_2NH + CS_2 \rightarrow R^1_2NCS_2^-\overset{+}{N}H_2R^1_2 \overset{CS_2}{\rightleftarrows} 2R^1_2NCS_2H \xrightarrow{R^2XCH=CH_2} R^1_2NCS\underset{\underset{S}{\|}}{C}HCH_2\underset{\underset{XR^2}{|}}{}$$

X = O, S.

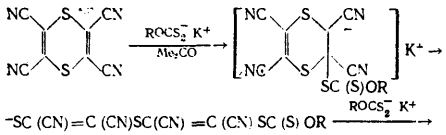
As expected, alkyl vinyl ethers proved to be more reactive in the reaction investigated than alkyl vinyl sulphides: the former react at 45–55 °C and the latter at 100 °C.

Numerous examples of the ionic addition of *O*-alkylxanthic acids to activated alkenes are known:[45-47]

$$R^1OCS_2H + R^2R^3=CHZ \rightarrow R^1OC(S)SCR^2R^3CH_2Z;$$
R^1 = Me, Et, n-Pr, iso-Pr, iso-Bu; R^2 = H, Me, Ph; R^3 = H, Me;
Z = COAlk, COAr, CO_2H, $CONH_2$, Ac.

Free xanthic acids are generated by treating the potassium salts with H_2SO_4.[45]

The reaction of potassium *O*-alkylxanthate with tetracyano-1,4-dithiine and tetracyanothiophen has been investigated.[48] Nucleophilic attack on the double bond is in this case always accompanied by ring opening with formation of compounds (V) and (VI):



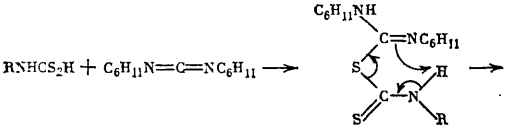
$$\rightarrow K^+ -SC(CN)=C(CN)SC(CN)=C(CN)SC(S)OR \xrightarrow{ROCS_2^-K^+} \rightarrow \underset{(V)}{(Z,E)\text{-}[K^+ -SC(CN)=C(CN)]_2S} + \underset{(VI)}{(ROCS)_2S}.$$

Like the reaction of dithiocarbamates, that of triethylammonium xanthate with dimethyl fumarate is reversible;[39] equilibrium is attained when 67% of the adducts (VII) has accumulated in the reaction mixture:

$$EtOCS_2^-\overset{+}{H}NEt_3 + (E)\text{-}MeO_2CCH=CHCO_2Me \rightleftarrows \underset{(VII)}{\rightleftarrows EtOC(S)SCH(CO_2Me)CH_2CO_2Me} + Et_3N.$$

In the case of a heterodouble bond (C=N), the reactions with dithiocarbamic acid proceed in a more complex manner, although here too the initial formation of the product of nucleophilic addition has been postulated.[49] Thus dithiocarbamic acid reacts with dicyclohexylcarbodiimide to form the isothiocyanate (VIII) and *NN'*-dicyclohexylthiourea (IX):

$$RNH_2 + CS_2 \rightarrow RNHCS_2H$$



$$\rightarrow \underset{(VIII)}{RN=C=S} + \underset{(IX)}{C_6H_{11}NHC(S)NHC_6H_{11}}.$$

When dimethyl azodicarboxylate was allowed to react with *O*-alkylxanthic acids, the product (X) of nucleophilic addition to the N=N bond was isolated:[45]

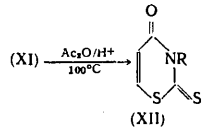
$$ROCS_2H + MeO_2CN=NCO_2Me \rightarrow \underset{(X)}{ROC(S)SN(CO_2Me)NHCO_2Me}.$$

2. The Addition of Dithiocarbamic and Xanthic Acids to Alkynes and Nitriles

Only alkynes activated by electron-accepting substituents react with dithiocarbamic acids. The reaction is exclusively ionic. Thus free dithiocarbamic acid and its *N*-monoalkyl derivatives, obtained from the ammonium salts *in situ*, add to the triple bond of propiolic acid and its esters at a low temperature with formation of *S*-vinyl esters of dithiocarbamic acid (XI):[14,50,51]

$$RNHCS_2^-\overset{+}{N}H_4 + HC\equiv C-CO_2R^1 \rightarrow \underset{(XI)}{(Z)\text{-}RNHC(S)SCH=CHCO_2R^1};$$
R, R^1 = H, Alk.

All the adducts of type (XI) obtained have the (*Z*)-configuration, cyclising to the corresponding 1,3-thiazines (XII) on heating in acetic anhydride in the presence of H_2SO_4:[14]



(XII)

The reactions of dithiocarbamic acid salts with non-activated alkynes have been widely investigated in recent years. The synthesis of *NN*-dialkyl-*S*-vinyl dithiocarbamates (XII) from acetylene, carbon disulphide, and secondary aliphatic amines in the presence of traces of KOH should probably be regarded as the first example of such reactions: [52,53]

$$HC{\equiv}CH + CS_2 + Alk_2NH \rightarrow \underset{(XIII)}{Alk_2NC(S)SCH{=}CH_2} .$$

It has been noted that the best yields of compound (XIII) (52–60%) are obtained at a pressure of 13–18 atm and 130 °C in DMF or water. [53]

A series of studies by Trofimov and co-workers on the interaction of dithiocarbamate anions with non-activated acetylenes have been a logical continuation of these investigations. [1–4,54] The reaction is carried out in polar aprotic solvents: dimethyl sulphoxide (DMSO), tetrahydrofuran (THF), hexamethylphosphoramide (HMP), and dioxan containing 1–6% of water. The reaction products are the corresponding *S*-vinyl esters of dithiocarbamic acids (XIII) and divinyl sulphides (XIV):

$$R^1_2NCS_2^-M^+ + R^2C{\equiv}CH \xrightarrow{H_2O} \underset{(XIII)}{(Z)\text{-}R^1_2NC(S)SCH{=}CHR^2} + \underset{(XIV)}{+ (Z,Z)\text{-}(R^2CH{=}CH)_2S} ;$$

$$R^1 = Alk;\ R^2 = H, Ph;\ M = Na, K .$$

The divinyl sulphides (XIV) are the products of secondary reactions of the *S*-vinyl esters (XIII): [1–4]

$$(XIII) + OH^- \rightarrow \begin{matrix} H \\ R^2 \end{matrix}\!\!>\!\!=\!\!<\!\!\begin{matrix} H \\ S^- \end{matrix} + [R^1_2NC(O)SH] \xrightarrow{R^2C{\equiv}CH}$$

$$\rightarrow \underset{(XIV)}{(Z,Z)\text{-}(R^2CH{=}CH)_2S} + R^1_2NC(O)S^- .$$

The divindyl sulphides (XIV) are formed especially readily in "superbasic media" (DMSO, H_2O, KOH solutions), where they become the main products. The best yields of the dithio-esters (XIII) have been obtained in THF in the presence of an excess of dithiocarbamate anions, at a moderate temperature, and for a long reaction time and also when buffer systems, preventing the accumulation of the base in the reaction mixture, were used. [54]

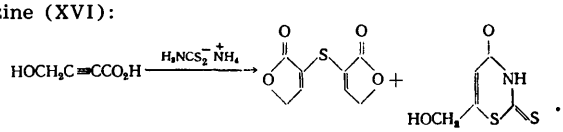
The reaction of the ammonium salts of dialkyldithiocarbamic acids with diacetylene leads to butenyne esters having exlusively the (*Z*)-configuration. [55] The reaction does not stop after the addition of one dithiocarbamate molecule:

$$R^2NCS_2^-\overset{+}{N}H_4 + HC{\equiv}C{-}C{\equiv}CH \xrightarrow{H^+} (Z)\text{-}HC{\equiv}C{-}CH{=}CH{-}SC(S)NR_2$$

$$\xrightarrow{R_2NCS_2^-\overset{+}{N}H_4} (Z,Z)\text{-}(Z,E)\text{-}R_2NC(S)SCH{=}CH{-}CH{=}CHSC(S)NR_2 .$$

Activated aceylenes also interact with dithiocarbamic acid salts. Thus the interaction of propiolic acid with dithiocarbamate anions at room temperature leads to low yields of the dithio-esters (XI), [56] which are also formed from *N*-alkyldithiocarbamic acids *in situ*. [14] All the adducts of type (XI) obtained have the (*Z*)-configuration. On heating in water in the presence of hydrobromic acid, the dithio-esters (XI) are converted into the (*E*)-isomers, while in the case of *N*-monosubstituted dithiocarbamic acids the dithio-esters (XI) cyclise to the 1,3-thiazines (XII). [56]

The main product of the interaction of ammonium dithiocarbamate with 4-hydroxy-2-butynoic acid is the divinyl sulphide (XV) together with a small amount of the 1,3-thiazine (XVI):



(XV), 30% (XVI), 6%

The reaction with the ethyl ester of this acid results in a significant increase in the yield of compound (XVI) (to 64%), but linear adducts have not been isolated in either the former or the latter case. [51]

According to Kishida and Terada, [57] the only products of the reaction of ammonium dithiocarbamate with functional derivatives of substituted and unsubstituted propiolic acid are the divinyl sulphides (XVII):

$$RC{\equiv}CX + H_2NCS_2^-\overset{+}{N}H_4 \rightarrow \underset{(XVII)}{(Z,Z)\text{-}(XCH{=}CR)_2S} ;$$

$$R = H, Me, Ph,\ X = CN, CO_2Et .$$

^1H NMR data demonstrate convincingly that the adducts (XVII) obtained have the (*Z*,*Z*)-configuration. On irradiation with UV light or on heating, the (*Z*,*Z*)-isomers are converted into the (*Z*,*E*)-form. The authors [57] explain the formation of (*Z*,*Z*)-divinyl sulphide (XVII) by the *trans*-nucleophilic addition to the triple bond. This view is shared by almost all investigators. [54–56] However, Cain and Warrener, [14] who carried out similar studies, believe that the configuration of the adducts does not indicate in this instance the preferential *trans*-addition of the sulphur-containing nucleophiles to the triple bond but reflect in reality merely the fact that the (*Z*)-isomer is more stable in the crystalline state.

In the reaction with tertiary propargyl chlorides, the dithiocarbamate anion initially substitutes the chlorine atom and only then adds to the triple bond. [58]

$$R^1_2NCS_2^-Na^+ + ClCR^2R^3C{\equiv}CH \xrightarrow[20°C]{H^+} \underset{(XVIII)}{(Z)\text{-}R^1_2NC(S)SCR^2R^3CH{=}CHSC(S)NR^1_2} ;$$

$$R^1 = Alk,\ R^2 = R^3 = Me;\ R^2 = H,\ R^3 = Me .$$

The product (XVIII) has the (*Z*)-configuration but isomerises on heating to 50 °C.

α-Acetylenic ketones react with *NN*-dialkyldithiocarbamic salts to form the corresponding *S*-vinyl dithio-esters (XIX), which are readily converted on heating into divinyl sulphides (XX): [59,60]

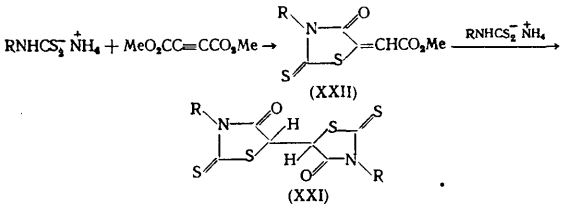
$$R^1_2NCS_2^-Cat^+ + R^2C{\equiv}CCOR^3 \rightarrow \underset{(XIX)}{R^1_2NC(S)SCR^2{=}CHCOR^3} \rightarrow \underset{(XX)}{(R^3COCH{=}CR^2)_2S} ;$$

$$R^1 = Alk;\ R^2, R^3 = H, Me, Ph;\ Cat = Na, K, NH_4 .$$

By carrying out the reaction in a two-phase system (water–diethyl ether), it is possible to avoid the charring of the products (XIX) and the formation of divinyl sulphide (XX). [59] The dithio-esters (XIX) are formed as a mixture of the (*Z*)- and (*E*)-isomers with the (*Z*)-isomer predominating. The appearance of the (*E*)-isomer, formally corresponding to the breakdown of the *trans*-addition rule, is due to the ease of the transition (*Z*) → (*E*). The decrease in the activation barrier to the isomerisation has been explained by the strong through-conjugation of the S–C=C–C=O system, which loosens the C=C bond. [1] When ammonium dithiocarbamate ($R^1 = H$) is introduced into the above reaction, the only product is the divinyl sulphide (XX). [60]

The nature of the products of the reactions of ammonium dithiocarbamates with dimethyl acetylenedicarboxylate (DMAD) depends significantly on the reaction conditions. In the

reaction of DMAD with an excess of ammonium *N*-alkyldithiocarbamate, the bisthiazolidinones (XXI) are formed. On the other hand, when the ammonium salt is added to an excess of DMAD, the reaction products are the thiazolidinones (XXII):[61]



(XXII)

(XXI)

The salts of *NN*-disubstituted dithiocarbamic acids react with acetylenecarboxylic acid esters regiospecifically and stereospecifically with formation of only the linear products (XXIII) (*trans*-nucleophilic addition) regardless of the electronic properties of the substituents at the nitrogen atoms and also of the nature of the cation and the solvent:[39,62,63]

$$R^1_2NCS_2^-Kat^+ + R^2C{\equiv}CCO_2Me \xrightarrow{H^+} (Z)\text{-}R^1_2NC(S)SCR^2{=}CHCO_2Me\ ;$$
(XXIII)

R^1 = Alk, $PhCH_2$; R^2 = H, CO_2Me, Ph; Kat = Na, $HNEt_3$.

In the presence of an excess of the dithiocarbamic salt, the adduct (XXIII) combines with a second dithiocarbamic acid molecule, forming a mixture of the *dl*- and *meso*-forms of the dimethyl esters of 2,3-bis(*NN*-dialkylthiocarbamoylthio)-succinic acid (XXIV):[39]

$$(Z)\text{-}R^1_2NC(S)SCR^2{=}CHCO_2Me + R^1_2NCS_2^-H\overset{+}{N}Et_3 \rightarrow$$
$$\rightarrow R^1_2NC(S)SCHR^2CH(CO_2Me)SC(S)NR^1_2\ ;$$
(XXIV)

R^1 = Et, R^2 = CO_2Me .

The non-stereospecificity of the addition of the second dithiocarbamic acid molecule is probably caused by the partial isomerisation of the adduct (XXIV) to the thermodynamically more stable diastereoisomer in the presence of the base. This hypothesis is confirmed by the results of a study of Angadiyavar et al.:[64] when DMAD was allowed to react with salts of secondary amines and *NN*-dialkyldithiocarbamic acids, only the thermodynamically more stable *erythro*-isomers of α-amino-β-dithiocarbamoylsuccinates (XXV) were found. In the first stage, the triple bond of DMAD is subjected to nucleophilic attack by the dithiocarbamate anion with formation of the monoadduct (XXVI). The formation of the diadduct (XXV) is a consequence of the addition of the secondary amine to compound (XXVI):

$$Alk_2NCS_2^-H_2\overset{+}{N}Alk_2 + MeO_2CC{\equiv}CCO_2Me \rightarrow Alk_2NC(S)SC(CO_2Me){=}$$
(XXVI)

$$={=}CHCO_2Me + HNAlk_2 \rightarrow Alk_2NC(S)SCH(CO_2Me)CH(CO_2Me)NAlk_2\ .$$
(XXV)

Acetylenic and diacetylenic compounds activated by the trifluoromethyl group (a σ-acceptor substituent) also interact with the triethylammonium salts of *NN*-dialkyldithiocarbamic acids regiospecifically and stereospecifically, forming only linear adducts of type (XXVII):[63,65]

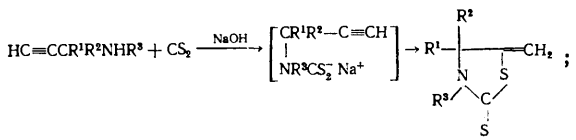
$$Alk_2NCS_2^-H\overset{+}{N}Et_3 + CF_3C{\equiv}CR \rightarrow (Z)\text{-}Alk_2NC(S)SC(R){=}CHCF_3 + NEt_3\ ;$$
(XXVII)

R = H, CF_3 .

The dithiocarbamate anion adds to trifluoromethyldiacetylenes contrary to the Markovnikov rule:[63]

$$Alk_2NCS_2^-H\overset{+}{N}Et_3 + CF_3C{\equiv}CC{\equiv}CR \rightarrow (Z)\text{-}Alk_2NC(S)SC(CF_3){=}$$
$$={=}CHC{\equiv}CR + NEt_3\ .$$

Apart from the intermolecular interaction of dithiocarbamates and acetylenes, there exist examples of the intramolecular nucleophilic addition of these salts to the triple bond:[66–69]



R^1, R^2, R^3 = H, Me, iso-Pr.

The yield is a maximum for R^3 = H.[67]

The addition of xanthic acid salts has been studied in less detail than for dithiocarbamates. Thus it has been noted that, like dithiocarbamates, the ethylxanthate anion interacts with non-activated acetylenes.[70] The main reaction product is the divinyl sulphide (XXIV), although under certain conditions it is possible to isolate the intermediate vinyl ester (XXVIII):

$$EtOCS_2^-\overset{+}{N}a + RC{\equiv}CH \rightarrow \underset{\text{(XXVIII)}}{EtOC(S)SCH{=}CHR} + \underset{\text{(XIV)}}{(Z,Z)\text{-}(RCH{=}CH)_2S}\ .$$

The addition of the xanthate anion to diacetylene in alcoholic solutions leads to the formation of the corrsponding vinyl acetylenic dithio-esters with the (*Z*)-configuration:[71]

$$ROH + CS_2 + HC{\equiv}C{-}C{\equiv}CH \xrightarrow[70^\circ C]{KOH} (Z)\text{-}ROC(S)SCH{=}CHC{\equiv}CH\ ;$$
R = Me, Et, Bu .

Activated acetylenes such as derivatives of acetylenecarboxylic acids also combine with alkylxanthates regiospecifically and stereospecifically to form the corresponding vinyl dithioesters (XXIX):

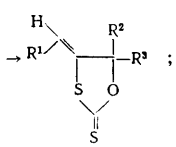
$$R^1OCS_2^-Kat^+ + R^2C{\equiv}CCO_2R^3 \rightarrow \underset{\text{(XXIX)}}{(Z)\text{-}R^1OC(S)SCR^2{=}CHCO_2R^3} \rightarrow$$
$$\xrightarrow{R^1OCS_2^-Cat^+} \underset{\text{(XXX)}}{R^1OC(S)SCHR^2CH(CO_2R^3)SC(S)OR^1}\ ;$$

R^1, R^3 = Alk; R^2 = H, CO_2Alk; Cat = NH_4, $HNEt_3$.

The adduct (XXIX, R^1 = Et, R^2 = CO_2Me) can react with a second xanthate molecule to form a 2 : 1 adduct of type (XXX).[39]

The reactions of carbon disulphide with substituted propargyl alcohols take place via a mechanism involving the intramolecular addition of xanthates to the triple bond:[72,73]

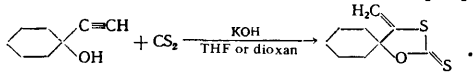
$$R^1C{\equiv}CCR^2R^3OH \xrightarrow{NaH} R^1C{\equiv}CCR^2R^3ONa \xrightarrow{CS_2} \underset{\text{(XXXI)}}{R^1C{\equiv}CCR^2R^3OCS_2Na} \rightarrow$$



(XXXII)

R^1 = H, Me, Ph, R^2, R^3 = H, Me, Et, n-Pr.

The intermediates (XXXI) can be isolated as the methyl esters after alkylation with methyl iodide.[74,75] Other experimental conditions for this reaction have also been proposed:[76]

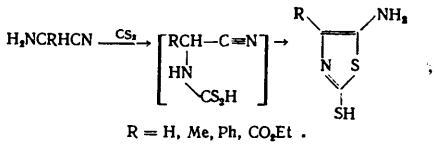


A single example of the interaction of potassium ethyl trithiocarbamate with phenylacetylene has been described in the literature.[77] This results in the formation of a mixture of the "usual" product (XXXIII) and the "anomalous" product (XXXIV) of the addition of the anion:

$$EtSCS_2^-K^+ + HC{\equiv}CPh \xrightarrow[THF/H_2O]{130^\circ C} \underset{\text{(XXXIV)}}{H_2C{\equiv}CPhSEt} + \underset{\text{(XXXIII)}}{(Z)\text{-}PhCH{=}CHSEt}\ .$$

There is also a possibility of intramolecular nucleophilic cyclisation with participation of the carbon–nitrogen triple bond. Thus it has been demonstrated[78–80] that the reaction

of carbon disulphide with α-aminonitriles leads to 5-amino-2-mercaptothiazoles:



R = H, Me, Ph, CO_2Et .

III. DITHIOCARBOXYLIC ACIDS

Derivatives of dithiocarbamic and xanthic acids have found extensive applications in industry. On the other hand, the chemistry of dithiocarboxylic acids RCS_2H, where R = aryl or alkyl, has been studied to a much lesser extent, for a number of reasons, than the chemistry of derivatives of dithiocarbamic and xanthic acids.[16–18] The compounds indicated differ significantly both from the related carboxylic and monothiocarboxylic acids. In the first place, the RCS_2H are stronger acids than the RCOSH and RCO_2H (the pK_a are 2.55, 3.33, and 4.75 respectively for R = Me [81]) and the character of their interaction with saturated compounds may be different.

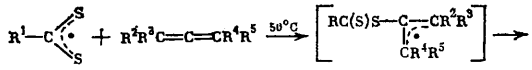
1. The Addition of Dithiocarboxylic Acids to Unsaturated Compounds

Examples of radical addition to unsaturated compounds do not exist for dithiocarbamic and other heterosubstituted dithio-acids. On the other hand, reactions involving radical addition to alkenes, dienes, allenes, and compounds with a strained double bond (norbornadiene) have been investigated in detail for aliphatic dithiocarboxylic acids.[9,82–85] The distinctive features of these reactions are as follows: dithiocarboxylic acids add to the double bonds of alkenes which have not been activated by electron-accepting substituents; the reaction is initiated in the presence of a source of free radicals and leads to the formation of not only the adducts (the corresponding dithio-esters) but also to cycloaddition products (see the next Section).

However, under certain conditions cyclisation may not in fact be observed. Thus the interaction of dithiobenzoic acid with styrene in the presence of azobisisobutyronitrile results in the exclusive formation of α-phenylethyl dithiobenzoate.[84] The introduction of a source of free radicals into the isoprene–dithioisobutyric acid system results in the formation of only a mixture of the dithio-esters (XXXV) and (XXXVI) [83]— the products of the 1,4-addition of the dithiocarboxylic acid to the olefin:

$$CH_2{=}CMeCH{=}CH_2 + \text{iso-Pr}CS_2H \xrightarrow{R^{\cdot}} \underset{\text{(XXXV)}}{\text{iso-Pr}C\,(S)\,SCH_2CMe{=}CHMe} + \underset{\text{(XXXVI)}}{Me_2C{=}CHCH_2SC\,(S)\,Pr\text{-iso}}.$$

The addition of dithio-acids to allenes under mild conditions (40–50 °C) leads to the vinyl dithio-esters (XXVII): [85]



$$\longrightarrow \underset{\text{(XXXVII)}}{R^1C(S)SC(CHR^4R^5){=}CR^2R^3}\ ;$$

R^1 = Me, Et; R^2=R^4=H, R^3R^5=$(CH_2)_6$; R^2=R^3=Me, R^4=R^5=H; R^2=R^3=R^4=H; R^5=Me .

The interaction of dithiocarboxylic acids with alkylacetylenes has been scarcely investigated, but there are data showing that the free-radical addition of dithioacetic acid (DTA) to 3-hexyne leads to a mixture of the (*Z*)- and (*E*)-vinyl dithio-esters (XXXVIII): [83]

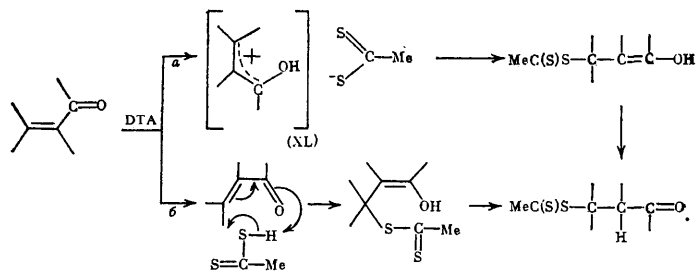
$$EtC{\equiv}CEt \xrightarrow[CCl_4(\text{boil})]{DTA} \underset{\text{(XXXVIII)}}{MeC\,(S)\,SCEt{=}CHEt}.$$

The familiar method of synthesis of dithiocarboxylic acid esters can be regarded as the first example of the thermal interaction of free dithiocarboxylic acids with alkenes activated by electron-accepting substituents: [17,87]

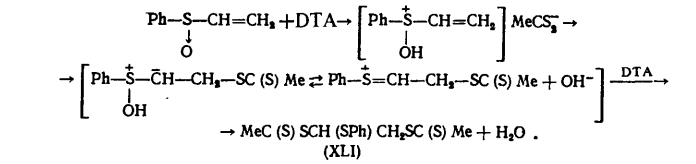
$$R^1CS_2H + R^2R^3C{=}R^4Z \rightarrow \underset{\text{(XXXIX)}}{R^1C\,(S)\,SCR^2R^3CR^4Z}\ ;$$

R^1 = Me, Et; R^2,R^3 = H, Alk, Ar, heteroaryl; R^4 = H, Me; Z = HCO, COR, CO_2H, CO_2Alk, CN, SOAlk, SO_2Alk, NO_2 .

In a study of the mechanism of this reaction, Oae et al.[88] proposed in 1972 two alternative versions, one of which (pathway *a*) presupposes the initial protonation of the electronegative group with formation of the intermediate (XLI) and the subsequent nucleophilic attack by the dithioacetate anion, while the other (pathway *b*) involves concerted addition:



It was found in the same study [88] that DTA can act as a reagent which reduces sulphoxides, sulphonium ylides, and sulphimides to the corresponding sulphides. Thus the reaction of DTA with phenyl vinyl sulphoxide leads to the product (XLI) of addition to the multiple bond with the simultaneous Pummerer rearrangement:



$$\rightarrow \underset{\text{(XLI)}}{MeC\,(S)\,SCH\,(SPh)\,CH_2SC\,(S)\,Me} + H_2O\ .$$

For alkenes with substituents incapable of being protonated with formation of intermediates of type (XL), the interaction with dithiocarboxylic acids leads to adducts in accordance with the Markovnikov rule:

$$CH_2{=}CR^1R^2 \xrightarrow{DTA} MeCR^1R^2SC\,(S)\,Me\ ;$$

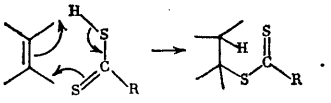
R^1 = H, Me; R^2 = Ph, OAlk, SAlk, OAc .

Vinyl esters and sulphides react much more readily than styrene.

Further studies [9,82–85] showed that the thermal (40–80 °C) addition of dithiocarboxylic acids to alkenes takes place fairly rapidly only when the double bond is activated by a neighbouring aromatic ring, carbonyl group, or heteroatom. In the case of simple alkenes, this is a very slow process even at about 120 °C. The presence of Lewis acids ($BF_3.Et_2O$) induces a faster, compared with a concerted process, ionic addition accompanied by rearrangements usual for reactions of this type, for example: [83]

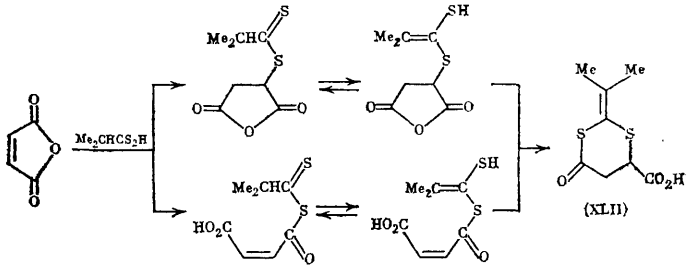
$$Me_2CH{-}CH{=}CH_2 \xrightarrow{A} MeC\,(S)\,SCH\,(Me)\,CHMe_2\ ,$$
$$\xrightarrow{BF_3Et_2O} MeC\,(S)\,SCMe_2CH_2Me\ .$$

The study of the thermal reaction in relation to deuterio-DTA showed[83] that (*Z*)-addition takes place. According to the authors,[83] the most probable mechanism of the thermal addition of dithiocarboxylic acids to alkenes involves a bimolecular reaction without an ionic or radical intermediate. Such addition may be most conveniently represented as a process occurring as a result of a concerted pericyclic shift (by analogy with "ene syntheses"):



Conjugation in the system increases its reactivity.

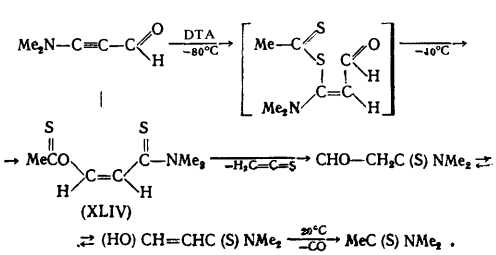
Maleic anhydride reacts with dithioisobutyric acid quantitatively, in the absence of catalysts, affording 1,3-dithiane (XLII). Presumably the addition begins in this case at the C=C bond and is followed by cyclisation via the enethiol form of the diothio-ester; however, Gressier and Levesque[9] do not rule out the possibility of the initial opening of the anhydride ring:



The reaction of DTA with propiolic acid at room temperature leads to a quantitative yield of the product (XLIII) of the Michael addition [a mixture the (*Z*)- and (*E*)-isomers in proportions of 6 : 4]. Methyl propiolate reacts with DTA in boiling CCl_4 and affords a mixture of the (*Z*)- and (*E*)-isomers of compound (XLIII) in proportions of 5 : 95; in the presence of Lewis acids, the isomer ratio is 25 : 75:[86]

$$HC{\equiv}CCO_2R \xrightarrow{DTA} MeC(S)S{-}CH{=}CHCO_2R\ ;\quad (XLIII)$$
$$R = H, Me\ .$$

The reaction of DTA with "push-pull" acetylene—a substituted ynamide—leads to an extremely unstable adduct, which rearranges to compound (XLIV) already at −40 °C. However, in contrast to the products of the addition of thiocarboxylic acids, the reaction does not stop at this point: on heating to room temperature, initially thioketen and then carbon monoxide are split off; the reaction product is thioacetamide:[89]



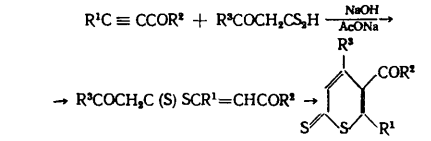
Several examples of the interaction of salts of dithiobenzoic acid with αβ-unsaturated ketones, which proceed with formation of adducts, have been described:[90]

$$PhCS_2MgBr + R^1R^2C{=}CHCOR^3 \rightarrow PhC(S)SCR^1R^2CH_2{-}COR^3\ ;$$
$$R^1, R^2 = H, Me, Ph;\ R^3 = Me, Ph$$

It has been noted that sodium dithiobenzoate is more reactive than the magnesium salt; it also reacts with benzoquinone and 1,2-dihydro-1-methylenenaphthalin-2-one.[90]

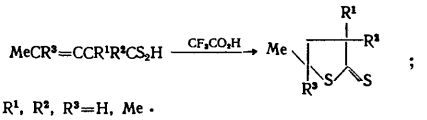
The interaction of triethylammonium dithiobenzoate with methyl propiolate in acetonitrile at −70 °C in the presence of an equimolar amount of acetic acid takes place stereoselectively as *trans*-addition with the preferential (>95%) formation of (*Z*)-PhC(S)−CH=CH.CO_2Me (overall yield 88%).[39]

The condensation of salts of β-ketodithiocarboxylic acids with DMAD[91] and α-acetylenic ketones[92] passes through a stage in which dithiocarboxylic acids add to the triple bond and leads to substituted thiopyrans; in a number of instances, the products of the Michael addition were isolated and characterised:[91]



R^1=CO_2Me, Ph; R^2=Me, OMe, Ph; R^3=Ar .

The reaction of αβ-unsaturated β-chloro-substituted aldehydes and ketones with aliphatic dithiocarboxylic acid apparently proceeds analogously.[92,93] The conversion of unsaturated tithiocarboxylic acids into γ-dithiolactones, described by Schonufts et al.,[94] can be regarded as an example of the intramolecular addition of dithiocarboxylic acids to the double bond:



R^1, R^2, R^3=H, Me .

There exist several examples of the interaction of dithiocarboxylic acids with heterounsaturated compounds. Thus the reactions of aromatic dithiocarboxylic acids with aryl isocyanates lead to the corresponding products of addition to the C=N bond:[95]

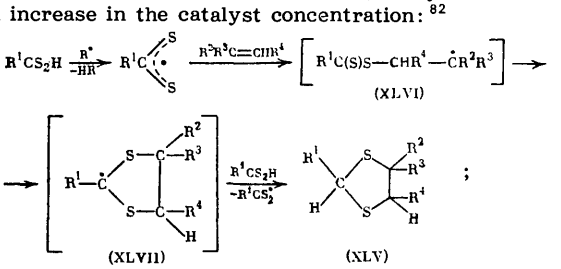
$$R^1CS_2H + R^2N{=}C{=}O \xrightarrow{EtONa} R^1C(S)SC(O)NHR^2\ .$$

Treatment of dicyclohexylcarbodiimide with DTA results in the formation of dicyclohexylthiourea and the unstable DTA anhydride:[49]

$$C_6H_{11}N{=}C{=}NC_6H_{11} \xrightarrow{2DTA} [MeC(S)]_2S + C_6H_{11}NHC(S)NHC_6H_{11}\ .$$

2. Cycloaddition of Dithiocarboxylic Acids to Unsaturated Compounds

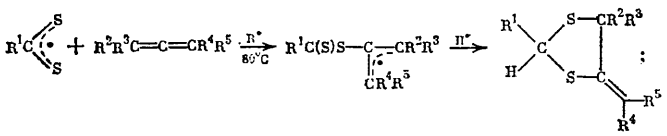
(a). Radical [3 + 2]cycloaddition. As was shown above, many adducts of dithiocarboxylic acids with unsaturated compounds can subsequently give rise to cyclic derivatives. However, in the presence of sources of free radicals, dithiocarboxylic acids can also enter directly into cyclisation reactions involving double bonds. Thus the interaction of DTA with styrene in the presence of azobisisobutyronitrile affords 1,3-dithiolans (XLV) and not dithioesters, the yield increasing with increase in the catalyst concentration:[82]



R^1=Alk; R^2=Ar; R^3=H, Me, Ph; R^4=H, Me .

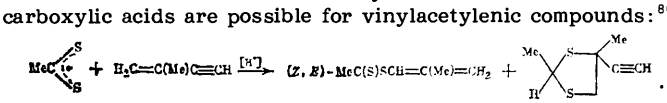
The use of deuterio-DTA in the reaction showed that deuteriation takes place exclusively at the C(2) atom of the dithiolan ring. A more detailed study showed[84] that the dithiolans (XLV) are formed preferentially in the reactions of alkenes having a phenyl substituent with aliphatic dithiocarboxylic acids. The cyclisation reaction (XLVI) → (XLVII) represents a non-trivial instance of thiophilic radical addition to the C=S bond.

The formation of 1,3-dithiolans is observed in the reactions of dithiocarboxylic acids with allenes in the presence of a source of free radicals and on refluxing in benzene:[85]

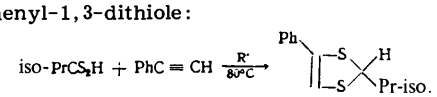


R^1=Me, Et; R^2=R^5=H, R^3R^4=$(CH_2)_6$; R^2=R^3=Me; R^4=R^5=H; R^2=R^3=R^4=H, R=Me.

Both free-radical addition and cycloaddition of dithiocarboxylic acids are possible for vinylacetylenic compounds:[86]

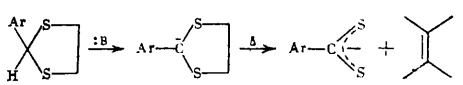


It was found in the same study[86] that the reaction of dithioisobutyric acid with phenylacetylene in the presence of azobisisobutyronitrile (on refluxing in benzene) affords 2-isopropyl-4-phenyl-1,3-dithiole:



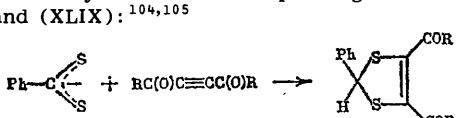
(b) Anionic [3 + 2]cycloaddition of dithioate anions. The anions of dithiocarboxylic acids are isoelectronic analogues of allyl anions. The cycloaddition of allyl anions to unsaturated compounds is known to be symmetry-allowed.[96] Although this reaction could not be achieved for the allyl anion itself, such cycloaddition is known for aza- and diaza-allyl anions[97] and a large group of αβ-unsaturated thioate anions and their selenium and tellurium analogues.[98]

A method of synthesis of aromatic dithiocarboxylic acids from 1,3-dithiolans was proposed in 1979:[99]



During recent years, this method has been used fairly widely to synthesise derivatives of trithiocarbonic acids[100–102] and also for the preparation of aliphatic dithiocarboxylic acids from 2-substituted 1,3-dithiolans.[103] The above syntheses are examples of anionic [3 + 2]cycloelimination. It was logical to suppose that, when the reactants and conditions have been chosen appropriately, it would be possible to achieve also the reverse reaction involving the anionic [3 + 2]cycloaddition of 1,3-dithia-allyl systems to multiple bonds.

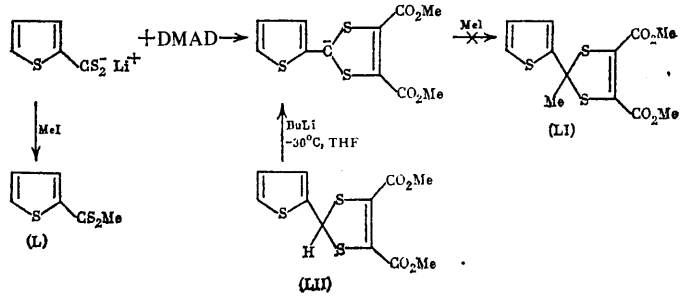
Indeed the reaction of triethylammonium dithiobenzoate with DMAD or dibenzoylacetylene in acetonitrile or methanol at room temperature yielded the corresponding 1,3-dithioles (XLVIII) and (XLIX):[104,105]



R=OMe (XLVIII), Ph (XLIX).

It has been suggested[106,107] that the 1,3-dipole reactivity is a common property of 1,3-dithia-allyl anionic systems. However, it was found unexpectedly that the nature of the group at the central carbon atom of the dithioate group has a decisive influence on the character of the adduct formed:

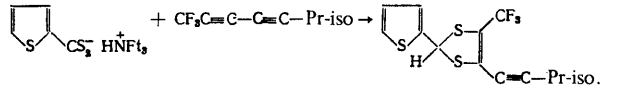
anions of aromatic or heteroaromatic systems (Ar = phenyl, 1-naphthyl, 2-thienyl, 2-furyl, or *N*-pyrrolyl) enter into the cycloaddition reaction.[39,62,105,106] On the other hand, the salts of dithiocarbamic and xanthic acids react with DMAD to form only the alternative adduct resulting from nucleophilic addition to the triple bond and the reaction proceeds exclusively stereospecifically as *trans*-addition.[39] The reaction depends little on the nature of the solvent, while the nature of the salt cation influences significantly its course. Thus the introduction into the reaction of the magnesium salt of naphthalene-1-dithiocarboxylic acid reduced the yield of the cycloadduct to 3–4% and the lithium salt of thiophen-2-dithiocarboxylic acid does not react at all with DMAD: alkylation with methyl iodide for 1 h leads to the formation of only the methyl ester of thiophen-2-dithiocarboxylic acid (L) and not to the expected 2-methyl derivative of 1,3-dithiole (LI):[63]



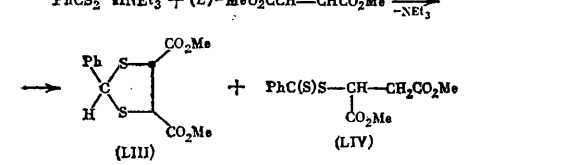
It has been demonstrated convincingly that the intermediate cyclic carbanion in the form of its lithium salt readily undergoes the reverse anionic [3 + 2]cycloelimination reaction; metallation of the 1,3-dithiole (LII) (obtained by the reaction of the triethylammonium salt of thiophen-2-dithiocarboxylic acid with DMAD) by butyl-lithium in THF at −30 °C and subsequent methylation with methyl iodide led to the subsequent detection in the reaction products, as in the previous case, of only the methyl ester of thiophen-2-dithiocarboxylic acid (L).[63]

Acetylenes whose triple bond has been activated on either side by electron-accepting (π or σ) substituents enter into the cycloaddition reaction: these are acetylenedicarboxylic acid esters, dibenzoylacetylene,[105] the methyl ester and nitrile of phenylpropiolic acid,[63] and hexafluorobutyne.[65]

Acetylenes whose triple bond has been activated by only one electron-accepting substituent react with the anions of dithiocarboxylic acids via the mechanism involving the ionic stereoselective *trans*-addition;[39] however, in the reaction of triethylammonium thiophen-2-dithiocarboxylate with trifluoromethylacetylene, the less stable cycloadduct was detected in the reaction medium together with the stable acyclic adduct. Only the cycloadduct was isolated in the reaction of the same salt with isopropyltrifluoromethyldiacetylene:[63]



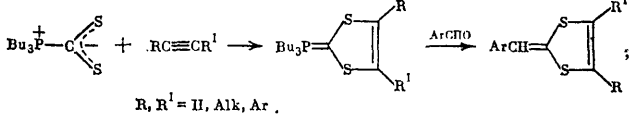
The reaction of triethylammonium dithiobenzoate with dimethyl fumarate takes place via two pathways with formation of both the product (LIII) of anionic [3 + 2]cycloaddition and the product (LIV) of nucleophilic Michael addition to the double bond in proportions of 2 : 1:[105]



Detailed study of the reaction mechanism showed that, under the reaction conditions, the adduct (LIV) cannot be converted into the cycloadduct (LIII) on treatment with a base, by-passing the stage involving decomposition into the initial components; this supports indirectly the concerted mechanism of the cycloaddition reaction.

The betaines formed by the reaction of phosphines with carbon disulphide and also the formamidinium and imidazolidinium dithiocarboxylates, obtained from the corresponding tetra-aminoethylenes and carbon disulphide, constitute unusual 1,3-dithia-allyl systems capable of anionic [3 + 2]-cycloaddition.

The adduct of carbon disulphide and tributylphosphine reacts with acetylene having electron-accepting substituents at temperatures as low as -30–0 °C; arylacetylenes react slowly at room temperature and acetylene itself reacts at temperatures above 100 °C with formation of the corresponding phosphorus ylides:[108,109]

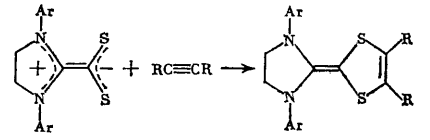


R, R^1 = H, Alk, Ar.

When aromatic aldehydes are introduced into the reaction mixture, the process terminates with the Wittig reaction. It is essential to note that ketones do not enter into this reaction.[109]

The reaction has since been widely used in the synthesis of varied 1,3-dithiole structures—2-substituted 1,3-dithioles [110] and tetrathiafulvalenes.[111,112] A fairly complete survey of the reactions of trialkyl (1,3-dithiolyl)phosponium tetrafluoroborates has been published in two reviews.[113,116]

Formamidinium and imidazolidinium dithiocarboxylates react analogously with doubly activated acetylenes,[117] for example

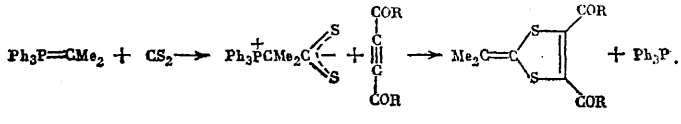


R = CO_2Alk, P(O)Ph_2, COPh; CF_3.

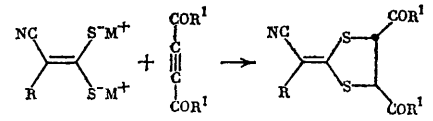
It is of interest that dipolarophile compounds having activated double bonds (tetracyanoethylene, dimethyl dicyanofumarate, dibenzyl azodicarboxylate) do not enter into the reaction.[118]

Betaines in which the 1,3-dithia-allyl system of the anion is separated from the positively charged centre by carbon atoms have been obtained by the reaction of triphenylphosphonium ylides with carbon disulphide.[119–121]

The 1,3-dithia-allyl system in the α-(triphenylphosphonia)-alkanedithiocarboxylates reacts with the triple bond activated on either side by electron-accepting substituents via the anionic [3 + 2]cycloaddition mechanism with formation of 2-alkylidene-1,3-dithioles; the fact which determines this course of the reaction is the subsequent stabilisation of the intermediate cyclic zwitter-ion as a result of the elimination of triphenylphosphine and the formation of an exocyclic double bond:[112,113]



The salts of 1,1-vinylidenedithioles are formed readily in the reactions of carbon disulphide and compounds having an active methylene group in the presence of bases. These salts, which can be regarded as salts of the dianions of the corresponding dithiocarboxylic acids, also react readily with doubly activated acetylenes, affording *trans*-4,5-disubstituted 2-alkylidene-1,3-dithiolans as the reaction products:[124–126]



R = CN, $CONH_2$, CO_2Et; R^1 = Alk, Ph.

The reactions involving the addition of dithio-acids to unsaturated compounds, examined above, are of undoubted interest also from the theoretical point of view apart from their practical and synthetic importance. Frequently a seemingly not very significant change in the details of the structures of the reactants and the reaction conditions leads to striking qualitative transitions from one mechanism to another, which are sometimes not easy to explain from modern theoretical standpoints.

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Rearrangements with Migration of a Fluorine Atom

L.S.Kobrina and V.N.Kovtonyuk

The review is devoted to the rearrangement of organic compounds and intermediate species involving the migration of a fluorine atom. The sigmatropic migrations of a fluorine atom are examined from the standpoint of modern theoretical ideas. Special attention has been given in this review to reactions proceeding with migration of a fluorine atom in intermediate species.
The bibliography includes 87 references.

CONTENTS

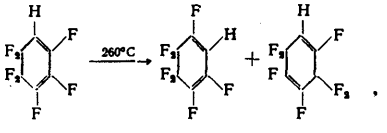
I. Introduction 62
II. Sigmatropic shifts of a fluorine atom in polyfluorinated olefins and cyclo-olefins 62
III. The migrations of a fluorine atom in carbenes, 1,3-biradicals, and radical-ions 64
IV. The migrations of fluorine atoms in radicals 65

I. INTRODUCTION

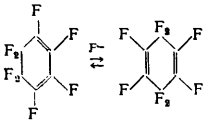
The rearrangements of organic compounds occupy an important place in organic chemistry, serving as a basis of many synthetic methods. In the vast stream of review publications devoted to a wide variety of aspects of rearrangements, much attention has been devoted to rearrangements with migration of halogen atoms in free radicals but there are virtually no reviews on the migration of a fluorine atom.[1] The latter factor is an obstacle to the development of a rigorous theory of reactions of this type, resulting in the propagation of the incorrect view that rearrangements with migration of a fluorine atom are impossible. The work by French investigators devoted to the theoretical study of free-radical rearrangements in which the authors explain the lack of experimental data concerning the 1,2-migration of a fluorine atom by the high barrier of such migration, may serve as an example of this situation.[2] On the other hand, numerous studies indicating the migration of a fluorine atom have been published in the last decade. The aim of the present review is to survey the available literature data on rearrangements with migration of a fluorine atom in a wide variety of situations and to make certain comparisons with the migrations of other halogen atoms, eliminating thereby the contradictions which have arisen between theoretical and experimental studies. The rearrangements in which the fluoride anion participates are not considered in detail in the present review.

II. SIGMATROPIC SHIFTS OF A FLUORINE ATOM IN POLYFLUORINATED OLEFINS AND CYCLO-OLEFINS

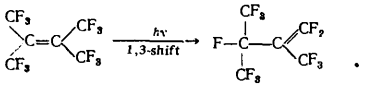
The isomerisation of polyflorinated olefins was first observed by Tatlow[3] in the pyrolysis of octafluorocyclohexa-1,4-diene and 1*H*-heptafluorocyclohexa-1,3-diene in a nickel flow-apparatus:



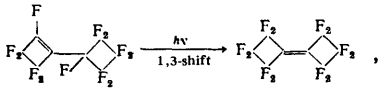
Later, in a study of the isomerisation of two octafluorocyclohexadienes,[4,5] it was shown that the establishment of equilibrium between the two dienes is accelerated by the fluoride anion and it was suggested that isomerisation thermolysis in nickel apparatus[3] also takes place with participation of the fluoride anion:



The photochemical migration of a fluorine atom has been noted in a series of polyflorinated olefins. Thus the photochemical 1,3-shift of a fluorine atom has been resorted to to account for the isomerisation of perfluoro-2,3-dimethylbut-2-ene:[6]



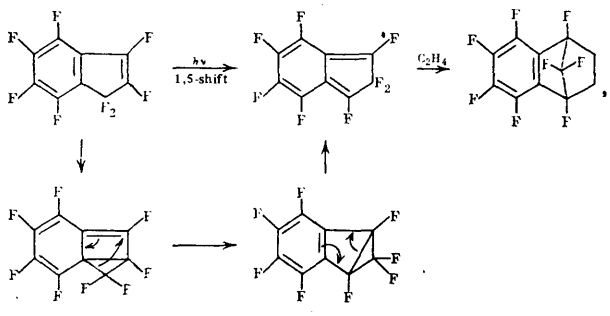
The 1,3-sigmatropic shift of a fluorine atom has been observed in the photolysis of perfluorinated cyclobutene derivatives:[7]



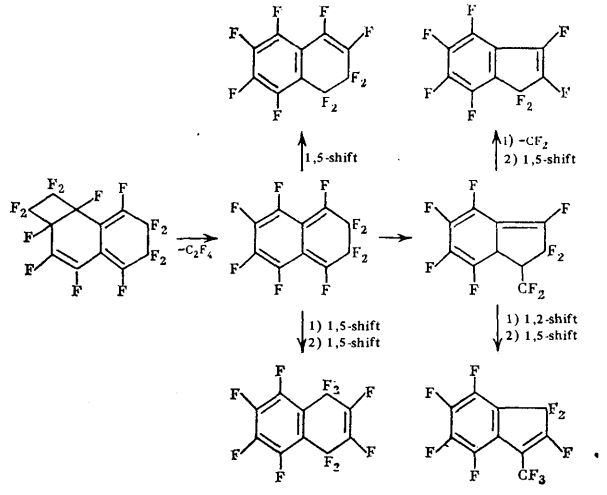
In a series of polycycloalkenes with dienes, the sigmatropic shift of a fluorine atom has been used to explain the isomerisation occurring both in photolysis and in thermolysis:[8-10]

Experimental confirmation of the sigmatropic migration of a fluorine atom in the photolysis of perfluoroindene has been explained—perfluoroisoindene is trapped in the form of an adduct with ethylene.[10] However, there is a possible alternative route to the formation of perfluoroisoindene which does

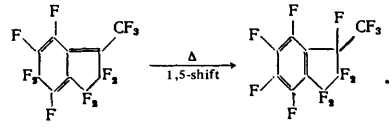
not require the invocation of a sigmatropic shift of a fluorine atom:[11]



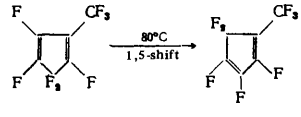
The formation of perfluorinated derivatives of 1,2- and 1,4-dihydronaphthalenes and perfluoroindenes in the thermolysis of perfluorinated bicyclictrienes has been explained by sigmatropic shifts of a fluorine atom:[12]



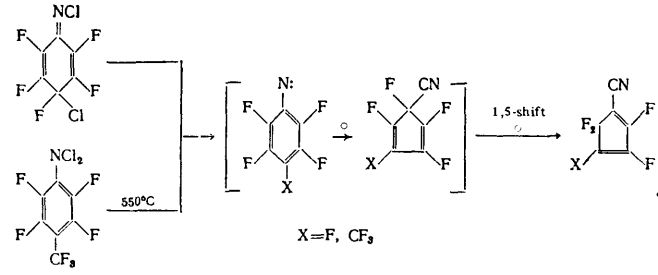
In the literature there are several further examples of thermal isomerisations involving a 1,5-sigmatropic shift of a fluorine atom. Thus, in the thermolysis of perfluoro-7-methylbicyclo[4.3.0]nona-1,4,6-triene, the migration of a fluorine atom leads to perfluoromethylindan:[13]



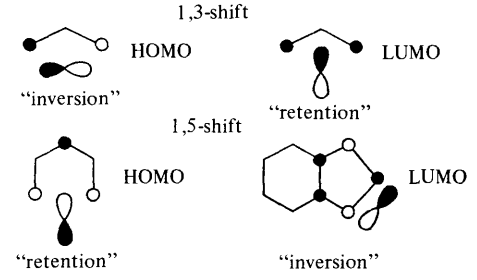
The sigmatropic migration of a fluorine atom has been observed in the thermolysis of perfluoro-2-methylcyclopentadiene:[14]



The 1,5-sigmatropic shift of a fluorine atom has also been invoked to account for the formation of polyfluorinated derivatives of cyclopentadiene in the thermolysis of the epoxy-derivatives of Dewar hexafluorobenzenes[15] and in the thermal isomerisation of perfluorinated arylnitrenes:[16,17]

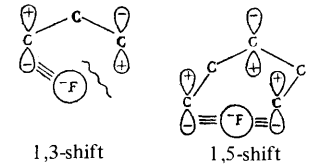


The great practical importance of isomerisations involving a sigmatropic shift of a fluorine atom in the chemistry of polyfluorinated olefins and cyclo-olefins led to attempts at a systematic and theoretical treatment of these processes. The sigmatropic shift of a fluorine atom has been discussed[5] from the standpoint of the theory of frontier orbitals. The frontier orbital approximation shows that, as for the migration of alkyl groups, the 1,3- and 1,5-shifts are allowed for a fluorine atom. The migration can be represented as the displacement of a fluorine atom in allyl or pentadienyl radicals:



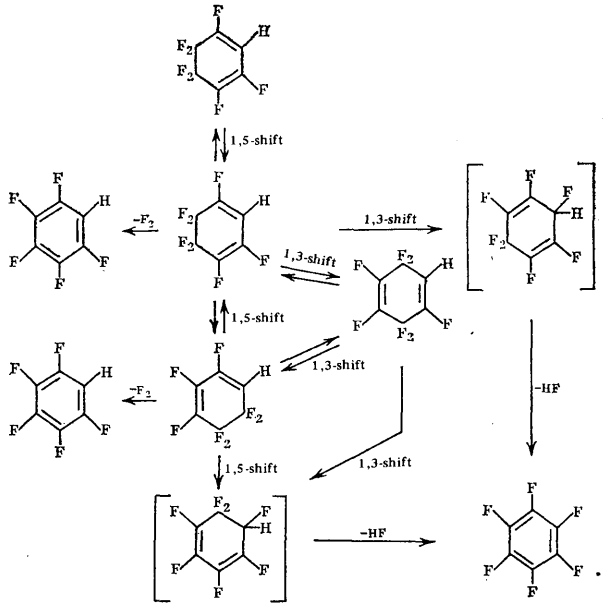
Two lobes of the atomic *p* orbital of the fluorine atom participate in the thermal 1,3-shift and the orbitals of the fluorine atom undergo "inversion" in the migration process. In the photochemical 1,3-rearrangement, occurring in the excited state, the configuration of the orbitals is retained. The rules are reversed for the 1,5-shift: for thermal reactions, the configuration of the orbitals is retained while for photochemical processes "inversion" should be observed.

It is believed[18] that the description of the migration of a fluorine atom within the framework of the sigmatropic shift can be complicated by the involvement of the unshared electron pairs of the fluorine atom. An approximate picture of this effect is secured by considering the migration of fluorine in the form of an anion, having spherical symmetry, in the allyl or pentadienyl cation. In this treatment, only the 1,5-shift is allowed from the standpoint of orbital interaction.

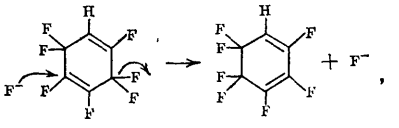


Indeed the pyrolysis of polyfluorocyclohexadienes shows that the 1,5-shift of a fluorine atom is preferred to the 1,3-shift.[18] However, these data cannot indicate the "prohibition" of the 1,3-shift of a fluorine atom. Analysis of the results presented at the beginning of this Section also demonstrates that the thermal 1,5-shifts[12-17] and the photochemical 1,3-shifts of a fluorine atom proceed more readily,[6,7] i.e. those processes in which the configuration of the orbitals of the fluorine atom should be "retained". A

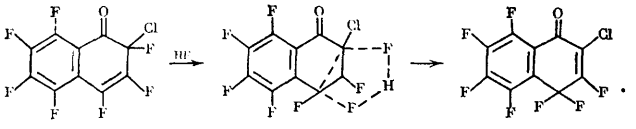
study of the interconversion of heptafluorocyclohexadienes led to the conclusion[5] that the fluorine atom migration processes occurring with "retention" of the configuration of the orbitals of the fluorine atom are preferable to those requiring the "inversion" of such configurations, although the extent of such preference is not high.



The results of the study by Burdon et al.[18] also show that the interpretation of the observed isomerisation invoking sigmatropic shifts of a fluorine atom should be approached with caution, since the 1,3- and also probably the 1,5-migration of a fluorine atom is catalysed by the fluoride anion:



Thus the results of the thermolysis of hepta- and octafluorocyclohexadienes in new Pyrex and quartz tubes differ appreciably from the results obtained in old tubes where more than 20 pyrolyses have been carried out. In pyrolyses in old tubes and also in pyrolyses in the presence of sodium fluoride, the 1,3-migration of a fluorine atom and the aromatisation of the initial dienes begin to proceed to an appreciable extent. Furthermore, fairly numerous examples of the HF-catalysed 1,3-migration of a fluorine atom are known in the literature.[19,20] Such an example is provided by the isomerisation of polyfluorinated cyclic dienones:



III. THE MIGRATION OF A FLUORINE ATOM IN CARBENES, 1,3-BIRADICALS, AND RADICAL-IONS

Numerous instances of the 1,2-shift of a fluorine atom in carbenes are known.[21,22] The observed series based on the capacity for migration[23] shows that hydrogen, chlorine, and the perfluoroalkyl group migrate more readily than the fluorine atom:[21,24] $Cl > H > C_2F_5 > F$.

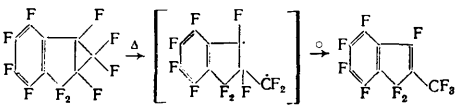
$$CF_3CH: \rightarrow CF_2{=}CHF ,$$
$$C_2F_5{-}CF_2CH: \rightarrow CF_2{=}CH{-}C_2F_5 .$$

In connection with the study of the vinylidene–acetylene rearrangement, much attention has been devoted recently to the possibility of the formation of difluoroacetylene in the isomerisation of difluorovinylidene:

$$CF_2{=}C: \rightarrow CF{\equiv}CF ,$$

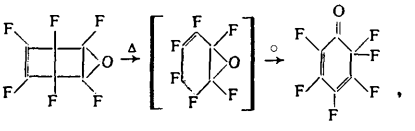
The corresponding calculations by various quantum-chemical methods have been described in a number of publications[25–26] and demonstrated the presence of a fairly high energy barrier (~36 kcal mol^{-1}) to the migration of a fluorine atom in this process, while a hydrogen atom migrates almost without a barrier in an analogous reaction.[26] The presence of a high barrier to the 1,2-migration of a fluorine atom has been attributed by Pople[26] to the antiaromatic character of the cyclic 4π-electron transition state. The high energy barrier to the 1,2-shift of a fluorine atom in this reaction is probably the reason why it has not so far been possible to effect experimentally the rearrangement of difluorovinylidene to difluoroacetylene.[28]

The 1,2-migration of a fluorine atom has been observed in the thermal isomerisation of perfluorocyclopropane derivatives with ring opening:[12,29]



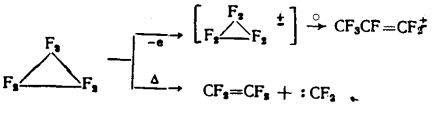
Perfluoromethylindene may be formed in the thermolysis of perfluorinated tricyclic cyclopropane derivatives both as a result of isomerisation wth the opening of the cyclopropane ring and subsequent 1,2-migration of a fluorine atom in the intermediate 1,3-biradical and synchronously.[29]

Perfluorocyclohexa-2,4-dien-1-one is formed similarly in the thermolysis of the epoxy-derivative of Dewar hexafluorobenzene,[15] which probably proceeds via the formation of the epoxy-derivative of hexafluorobenzene:



In contrast to the thermal reactions of perfluorocyclopropane derivatives quoted above, it has been suggested that cyclohexadienone is formed from the epoxy-derivative of Dewar hexafluorobenzene as a result of the migration of a fluorine atom in the zwitter-ion.[15]

A rearrangement with migration of a fluorine atom has been observed in the photoionisation of perfluorocyclopropane:[30]

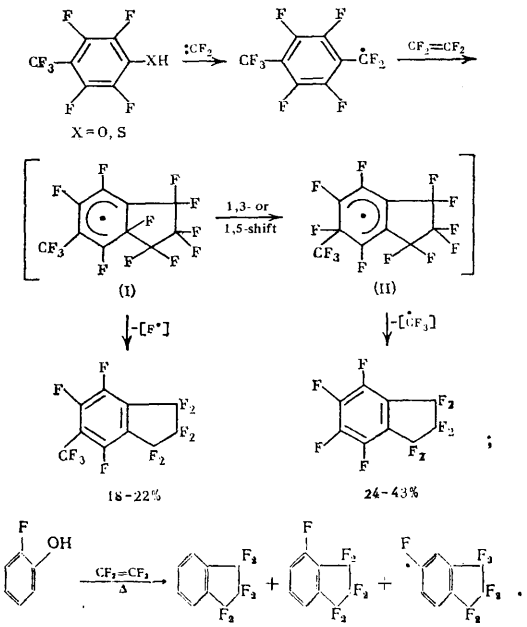


It is noteworthy that the thermolysis of perfluorocyclopropane does not lead to the formation of perfluoropropene but is accompanied by decomposition to tetrafluoroethylene with elimination of difluorocarbene.[31]

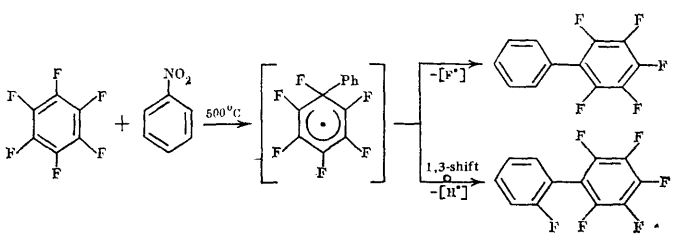
IV. THE MIGRATIONS OF FLUORINE ATOMS IN RADICALS

1. The 1,3- and 1,5-Shifts in Cyclohexadienyl Radicals

In order to account for the preferential formation of perfluoroindan in the copyrolysis of perfluoro-*p*-cresol and perfluoro-*p*-thiocresol with tetrafluoroethylene,[32] a mechanism has been proposed according to which a 1,3- or 1,5-sigmatropic shift of a fluorine atom takes place in the corresponding σ-complexes (I) with formation of the isomeric σ-complex (II). The stabilisation of the σ-complex (II) with abstraction of the trifluoromethyl radical leads to perfluoroindan. An analogous mechanism has been proposed also to explain the formation of 1,1,2,2,3,3,5-heptafluoroindan together with hexafluoroindan and 1,1,2,2,3,3,4-heptafluoroindan in the copyrolysis of *o*-fluorophenol with tetrafluoroethylene in proportions of 1 : 2.5 : 2.2 respectively:[33]

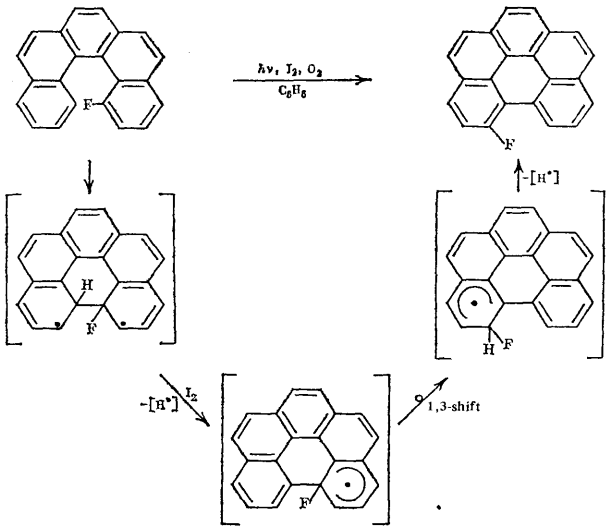


It has been suggested that the migration of a fluorine atom occurs also in the high-temperature reaction of nitrobenzene with hexafluorobenzene[34] in which 2,2',3,4,5,6-hexafluorobiphenyl was detected mass-spectrometrically:

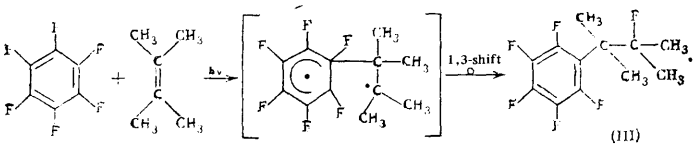


The formation of the same product has been detected in the reaction of benzoyl peroxide with hexafluorobenzene.[35]

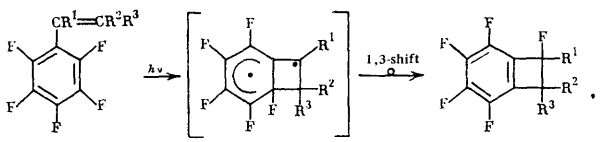
A similar migration of a fluorine atom has been proposed recently to account for the mechanism of the photocyclisation of 1-fluoro[5]helicene:[36]



The photolysis of hexafluorobenzene in the presence of 2,3-dimethylbut-2-ene leads mainly to the product (III), whose formation is apparently associated with the 1,3-migration of a fluorine atom from the ring to the side chain in the intermediate biradical:[37]

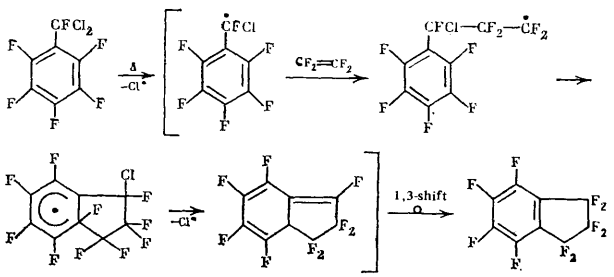


The migration of a fluorine atom has also been observed in the photocyclisation of polyfluorinated alkenylbenzenes in the gas phase,[38] leading to the formation of fluorine-containing benzocyclobutenes:



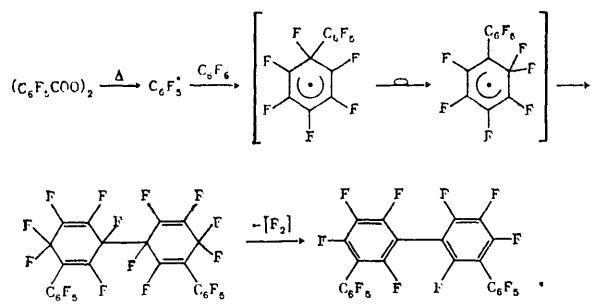
The migration of a fluorine atom can occur as a 1,3-sigmatropic shift concerted with the cyclisation process or following the latter, although the authors do not rule out the possibility of a repeated 1,5-shift of a fluorine atom.

Similar cyclisation with migration of a fluorine atom to the side chain has been observed also in the copyrolysis of pentafluoro(trichloromethyl)benzene with chlorotrifluoroethylene[39] and of αα-dichlorohexafluorotoluene with tetrafluoroethylene:[40]

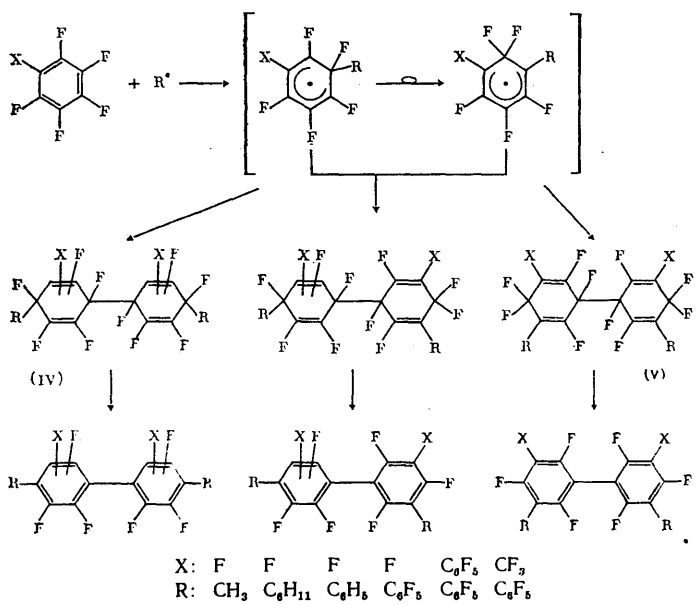


2. The 1,2-Migration of a Fluorine Atom in Cyclohexadienyl Radicals

Ten years ago the 1,2-migration of a fluorine atom in radicals was still regarded as impossible.[41] During the intervening period, a series of studies providing experimental evidence that such migration is achievable under certain conditions have been published. The 1,2-migration of a fluorine atom in cyclohexadienyl raidcals, formed in the radical reactions of aromatic polyfluoro-compounds, has been studied in greatest detail. The rearrangement of cyclohexadienyl radicals with migration of a fluorine atom was first observed in a study of the interaction of hexafluorobenzene with pentafluorobenzoyl peroxide at 200 °C.[42] The defluorination of the mixture of products of this reaction having the composition $C_{24}F_{22}$ led to the formation of perfluoro-*mm'*-quaterphenyl in a quantitative yield, which provided grounds for the assumption that its precursor is perfluoro-3,3'-diphenyl-1,1',4,4'-tetrahydroquaterphenyl—the dimer of the σ-complex resulting from the addition of the pentafluorophenyl radical to hexafluorobenzene. Evidently, this dimer cannot be obtained by the dimerisation of the primary σ-complex but is the product of the dimerisation of the secondary σ-complex formed on rearrangement with migration of a fluorine atom from the geminal site in the cyclohexadienyl radical to a neighbouring position:

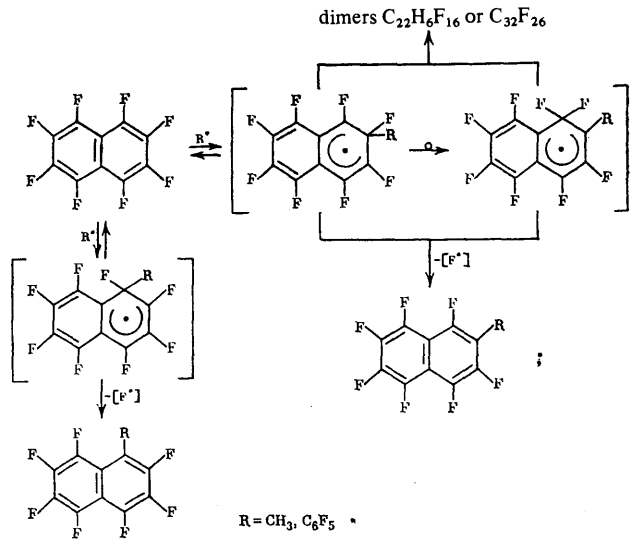


An analogous rearrangement takes place in the cyclohexadienyl radical formed in the reaction of hexafluorobenzene with phenyl,[43] methyl,[44] and cyclohexyl[45] radicals and also in the reactions of octafluorotoluene[46] and decafluorobiphenyl[47] with the pentafluorophenyl radical:



X: F F F F C_6F_5 CF_3
R: CH_3 C_6H_{11} C_6H_5 C_6F_5 C_6F_5 C_6F_5

In the cyclohexadienyl radicals formed by the addition of perfluoroalkyl radicals[44,48,49] or the pentafluorobenzoyloxy-radical[42,50] to aromatic polyfluoro-compounds, a rearrangement with migration of a fluorine atom does not take place. The general character of the rearrangement of polyfluorinated cyclohexadienyl radicals with 1,2-migration of a fluorine atom has been confirmed by the results of the reaction of octafluoronaphthalene with the methyl and pentafluorophenyl radicals:[51]



A characteristic feature of these reactions is a relatively high yield of 2-substituted octafluoronaphthalene derivatives, which can be attributed to the reversible addition of the methyl and pentafluorophenyl radicals to the aromatic ring and the consequent possibility of the interconversions of the isomeric σ-complexes. The irreversible removal from the equilibrium of the σ-complexes formed when these radicals are added to the 2-position in octafluoronaphthalene, as a result of a rearrangement with migration of a fluorine atom from the geminal site in the cyclohexadienyl radical to the 1-position, ensures the accumulation of more stable σ-complexes, whose defluorination actually affords 2-substituted heptafluoronaphthalenes.

A kinetic scheme for the interaction of aromatic polyfluoro-compounds with radicals has been analysed for the reaction of hexafluorobenzene with the cyclohexyl radical.[45] It follows from this analysis that the rearrangement is a unimolecular process, since the ratio of the yields of the products (IV)/(V) (see the scheme above) is a linear function of the concentration of the cyclohexyl radical R', which depends on the initial concentration c_0 of the source of this radical:

$$(IV)/(V) = K[R^{\cdot}] = f(c_{0\ \text{peroxide}}).$$

The analogous analysis performed on the assumption of a bimolecular rearrangement gives rise to the ratio (IV)/(V) which is independent of the radical concentration. The experimental data show that in reality the product ratio (IV)/(V) varies with the concentration of di-t-butyl peroxide.

The dependence of the degree of rearrangement on the reaction temperature and the concentration of the source of the radical has been established for the interaction of hexafluorobenzene with the phenyl, pentafluorophenyl, and cyclohexyl radicals.[44] An increase in the reaction temperature increases the degree of the rearrangement. With an increase in the concentration of the source of the radical,

the lifetime of the radical σ-complexes diminishes as a result of the increase in their concentration in solution and there is a consequent decrease in the degree of rearrangement.

Assessment of the role of factors associated with the structure of the geminal site in polyfluorinated cyclohexadienyl radicals in a rearrangement with migration of a fluorine atom has shown that the possible contribution by the steric hindrance in the geminal site of the σ-complexes is extremely insignificant. The influence of the concentration of the source of the radical on the degree of rearrangement is the same for the σ-complexes formed by the addition to hexafluorobenzene of both the methyl and cyclohexyl radicals, which have similar polarities, but differs appreciably as regards its steric requirements[44] (See Table).

Estimation of the contribution of steric effects to the driving forces of the rearrangement.[44]

Concentration of di-t-butyl peroxide, M	Degree of rearrangement	
	$CH_3^{\cdot}$	cyclo-$C_6H_{11}^{\cdot}$
0.77	0.29	0.27
0.42	0.50	0.32
0.38	0.58	0.47
0.33	0.85	0.58
0.19	1.12	0.68

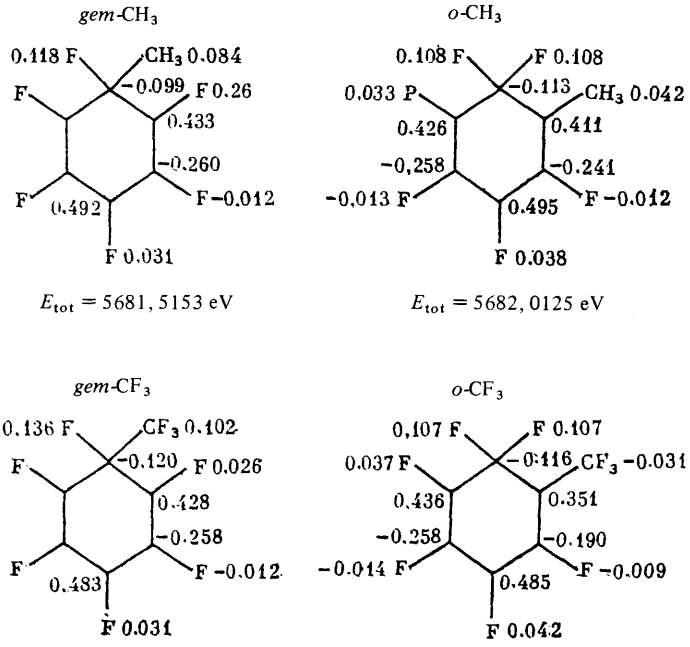
In order to estimate the influence of the nature of the substituents at the geminal site on the stability of the radical σ-complex, the total energies E_{tot} and the distribution of the spin densities in the rearranged and non-rearranged σ-complexes of the methyl and trifluoromethyl radicals with hexafluorbenzene were calculated.[44] The calculations were performed by the unrestricted Hartree–Fock method in terms of the INDO approximation with the standard parametrisation of Pople and Segal.[52] The bond lengths and angles optimal for fluorinated cyclohexadienyl radicals, obtained[53] by INDO calculations with the same parametrisation, were used.

The results of the calculation (see Figure), show that, when the methyl radical adds to hexafluorobenzene, the rearranged σ-complexes are more stable than the non-rearranged complexes by 11.6 kcal mol^{-1}, whereas in the case where hexafluorobenzene is attacked by the trifluoromethyl radical, the reverse situation obtains—the non-rearranged σ-complexes are found to be more stable (by 3.8 kcal mol^{-1}).

The ratio of the unpaired electron densities in various positions in the unsaturated part of the non-rearranged σ-complexes of the methyl and trifluoromethyl radicals with hexafluorobenzene are virtually the same, whereas for the geminal sites appreciable differences are observed on passing from the non-rearranged σ-complexes to the rearranged complexes: when the methyl radical adds on, a greater fraction of the spin density is found to be concentrated on the fluorine atoms of the difluoromethylene group at the geminal site, whereas in the case where the trifluoromethyl radical is added the fraction of spin density on the fluorine atoms of the geminal site is smaller than in the non-rearranged σ-complex.

Thus the results of the calculations show that the rearrangement may be caused by the energy gain on formation of the geminal unit with two fluorine atoms. The increase in the C–F bond strength as the geminal fluorine atoms accumulate has been described in the literature[54] and there exist data indicating the higher stability of the polyfluorinated arenium ions having two fluorine atoms in the geminal unit compared with isomers containing in the geminal unit substituents other than fluorine atoms.[55]

Although the difluoromethylene group is saturated, nevertheless it exhibits an electron deficient character.[56] For example, perfluoroalkanes form complexes with electron-donating solvents.[57] In the analysis of the electronic effect of the difluoromethylene group, Liebman used these data to justify treating it as an analogue of the carbonyl group.[58]



E_{tot} = 5681, 5153 eV E_{tot} = 5682, 0125 eV

E_{tot} = 7777, 9177 eV E_{tot} = 7777, 7468 eV

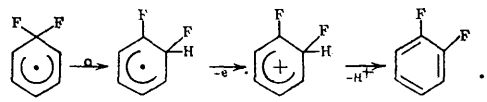
Distribution of spin density and total energies of polyfluorinated cyclohexadienyl radicals.[44]

If this approach is applied to the analysis of the stability of radical σ-complexes, then in the case where the geminal unit contains two fluorine atoms, the σ-complex can be regarded as a substituted phenoxy-radical after the replacement of the difluoromethylene group by the carbonyl group. The relatively high stability of different substituted phenoxy-radicals has long been known.[59]

In those cases where the geminal unit contains a fluorine atom and a substituent with a high electronegativity (perfluoroalkyl and pentafluorobenzoyloxy-groups), the electron-accepting properties of the unit produced remain extremely powerful. There exist literature data demonstrating the capacity of the trifluoromethyl group for conjugation with the radical centre.[60] On the other hand, the replacement of a fluorine atom in the difluoromethylene unit of a polyfluorinated radical σ-complex by an electron-donating substituent (the methyl or cyclohexyl group) should apparently lead to a sharp weakening of the electron-accepting properties of the saturated unit. These differences do in fact determine to some extent the possibility of the rearrangement of fluorinated radical σ-complexes with migration of a fluorine atom from the geminal unit to a neighbouring position.

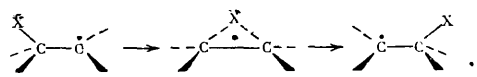
Burdon and Parsons[61] invoked the 1,2-shift of a fluorine atom in radical σ-complexes to explain the formation of fairly large amounts of aromatic polyfluoro-compounds in the reaction of benzene with $CsTlF_4$. Their calculation of the energy

of the cyclohexadienyl radicals by the CNDO/2 method showed that the stage involving the 1,2-migration of the fluorine atom is exothermic.

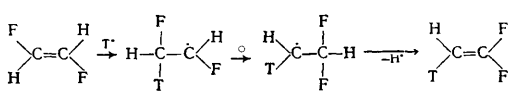


The authors believe that this is a key stage in the fluorination of aromatic compounds despite the fact that, in their view, it is prohibited from the standpoint of orbital symmetry rules. However, such prohibition tends to be regarded as absolute. The driving force of the rearrangement can apparently have a purely thermodynamic nature associated with the fact that the radical formed as a result of the rearrangement is much more stable than the initial radical.

In 1981 French workers published a theoretical study[2] of free-radical migration. They carried out a calculation by the STO-3G RHF method for a series of 1,2-rearrangements of β-substituted ethyl radicals. The difference between the energies of the β-substituted ethyl radical and the symmetrical bridge structure, adopted as the transition state in the process, was adopted as the energy barrier to the reaction:

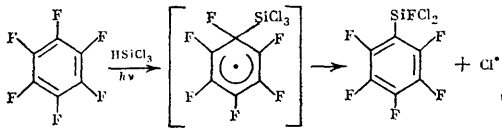


The calculation for the 1,2-shift of a fluorine atom, like that for the 1,2-shift of a hydrogen atom and groups such as OH, NH_2, and CH_3 yielded a very high barrier to the reaction (F = 107 kcal mol^{-1}, H = 88 kcal mol^{-1}). The authors believe that the activation energies for these rearrangements are much higher than the activation energies for processes such as recombination, transfer, etc. and that this is the reason why these rearrangements have not been detected experimentally. The authors were probably unaware of either the results of studies on the radical reactions of aromatic polyfluoro-compounds,[42-51] discussed above, or of a study[62] of the 1,2-shift of a fluorine atom in the 1,2-difluoroethyl radical obtained as a result of the addition of tritium to *trans*- and *cis*-1,2-difluoroethylenes:



It is also noteworthy that the method employed by Fossey and Nedelec[2] yields barriers to the rearrangements which are much too high. A calculation has been recently carried out for the 1,2-migrations in free radicals by the MNDO SCF-MO method.[63] The barriers to the rearrangement calculated in the above study are much lower than in the previous investigation[2] and agree with experimental data for rearrangements known in the literature. Unfortunately, the authors[63] did not carry out a calculation for the 1,2-migration of a fluorine atom.

In the literature, there are several further examples involving the 1,2-migration of a fluorine atom in reactions which can proceed via the formation of free radicals. Thus the photochemical interaction of hexafluorobenzene with trichlorosilane[64] leads mainly to dichlorofluoro(pentafluorophenyl)-silane:



It has been suggested that the formation of this product is associated with a rearrangement in the initial σ-complex of the trichlorosilyl radical with hexafluorobenzene. It was later shown that such rearrangement is a common reaction in the series of organosilicon compounds:[23]

$$ClCH_2CF_2SiCl_3 \xrightarrow{\Delta} ClCH_2CFClSiFCl_2 \xrightarrow{\circ} ClCH_2CCl_2SiF_2Cl\ .$$

The photochemical exchange of hydrogen and fluorine atoms is observed in the photolysis of isomeric difluoroethylenes:[65]

$$CFH{=}CFH \underset{}{\overset{h\nu}{\rightleftarrows}} CF_2{=}CH_2\ .$$

The mechanism of such exchange has not so far been investigated.

3. Comparison of the 1,2-Migration of a Fluorine Atom with the 1,2-Migration of Other Halogen Atoms

In contrast to the 1,2-migration of a fluorine atom, the 1,2-migration of other halogen atoms, in particular chlorine and bromine, in radicals is well known. Thus the 1,2-migration of a chlorine atom in alkyl radicals is very common:[1,66,67]

$$XCCl_2\dot{C}YCH_2Z \xrightarrow{\circ} X\dot{C}ClCClYCH_2Z\ ,$$
$$X{=}H,\ F,\ Cl,\ CH_3\quad Y{=}H,\ Cl,\ Br,\ CH_3\quad Z{=}Br,\ CCl_3,\ SR\ .$$

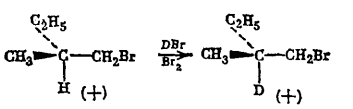
The data accumulated permitted the claim that this migration takes place intermolecularly and theoretical calculations[2,65] have shown that the 1,2-migration of a chlorine atom proceeds via a bridged transition state with a relatively low energy barrier (26.4 kcal mol^{-1}).[65] A series based on the relative stabilities of the radicals has been constructed,[6,7] its left-hand side coinciding with the familiar series based on the relative stabilities of hydrocarbon radicals (primary < secondary < tertiary):

$$RCH_2 < R_2CH < R_3C < RCHCl < R_2CCl < RCCl_3\ ,$$

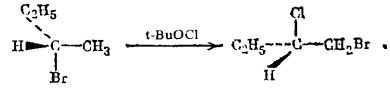
It is noteworthy that in the case of possible competition between the 1,2-shifts of a chlorine or a fluorine atom, the shift of a chlorine atom always takes place:[68,69]

$$CH_2{=}CH{-}CCl_2F + \dot{C}Cl_3 \rightarrow CCl_3CH_2\dot{C}HCCl_2F \xrightarrow{\circ}$$
$$\rightarrow CCl_3CH_2CHCl\dot{C}ClF \xrightarrow{t\text{-}BuNO} CCl_3CH_2CHClCClF{-}N(O\cdot){-}Bu\text{-}t.$$

The 1,2-migration of a bromine atom in alkyl radicals occurs at even higher rates than the migration of chlorine. Analysis of literature data[70] has led to the conclusion that the rates of these rearrangements can reach values >10^8 s^{-1} for chlorine and >10^{10} s^{-1} for bromine. The 1,2-migration of a bromine atom is not as common a process as the 1,2-migration of a chlorine atom probably because the β-bromoradicals can decompose fairly readily with formation of unsaturated compounds. The problem of "bridged" radicals is very closely related to the problem of the mechanism of the 1,2-migrations of bromine and chlorine atoms. It has been shown that in radical reactions of bromoalkanes the bromine atom is involved in anchimeric cooperation with the abstraction of a β-hydrogen atom.[1,70] This is manifested, for example, in radical reactions of optically active bromoalkanes. Thus the deuterium exchange reaction involving (+)-(*S*)-1-bromo-2-methylbutane proceeds with full retention of optical activity:[70]

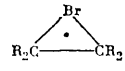


Asymmetry can be fully retained also in processes accompanied by the 1,2-migration of a bromine atom, for example, in the chlorination of (+)-(*S*)-2-bromobutane:[70,71]



Like the bromine atom, the chlorine atom is also involved in anchimeric assistance in the abstraction of a β-hydrogen atom, although to a lesser extent than bromine. Thus the racemisation of the intermediate chloroalkyl radical takes place to an appreciable extent in the bromination of (+)-(*S*)-1-chloro-2-methylbutane.[70] Similar anchimeric assistance has not been detected for the fluorine atom. The radical fluorination of (+)-(*S*)-1-fluoro-2-methylbutane leads to complete racemisation.[70]

These results can be explained by the formation in the intermediate β-bromo- and β-chloro-radicals of a bridged structure in which the rotation about the C_α–C_β bond is to a large extent hindered and the stabilisation of such a radical leads to the retention of asymmetry in the reaction products.



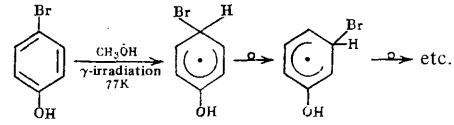
Analysis of the EPR spectra of β-chloroethyl radicals showed that the chlorine atom is in the eclipsed conformation with respect to the *p* orbital of the radical centre. Hence, it has been suggested that the radical has an asymmetric bridged structure.[72,73] In the β-fluoroethyl radical, the angle between the *p* orbital and the C–F bond is 50°.[72,74] These data agree with calculations by the MNDO method.[75] The different structures of the β-chloroethyl and β-fluoroethyl radicals are caused, according to the authors, by a combination of steric and electronic factors.[72,75]

Hudson[76] estimated from the standpoint of the perturbation theory the stabilisation of radicals as a result of bridge formation for β-halogenethyl radicals:

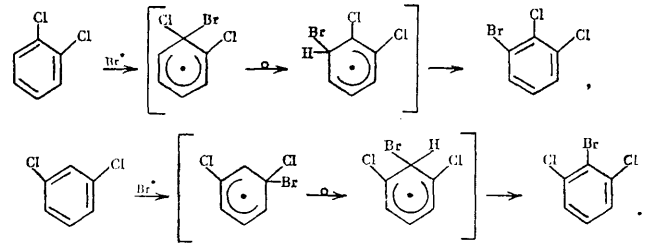
$-\Delta E$ (kcal mol^{-1}): I (7.54) Br (2.97) Cl (0.22) F (— 1.30) O (—0.72) .

These data show that bridge formation is unfavourable for fluorine and oxygen atoms. According to the author, this is caused mainly by the large difference between the energies of the interacting orbitals, which diminishes on passing from fluorine to bromine and iodine. The ease of the 1,2-migration of a halogen atom varies in the same direction. Thus it is apparently possible to distinguish three energy factors influencing the ease and direction of the 1,2-migration of a halogen atom: (1) the degree of interaction of the *p* orbital of the radical centre with the halogen atom; (2) the dissociation energy of the C–Hal bond in the β-halogenoethyl radical, which decreases from fluorine to bromine (46.3 kcal mol^{-1} for fluorine, 22.0 kcal mol^{-1} for chlorine, and 7.9 kcal mol^{-1} for bromine[2]); (3) the relative stabilities of the radicals formed.

Several examples of the migration of bromine and chlorine atoms in cyclohexadienyl radicals are also known. Thus the γ-irradiation of methanol solutions of bromobenzene and *p*-bromophenol at 77 K generates cyclohexadienyl radicals with bromine atoms in the geminal unit.[77] Analysis of the EPR spectra of these radicals shows that the bromine atom "rotates" around the ring via a rapid 1,2-shift (the lifetime in this state is $<10^{-7}$ s):

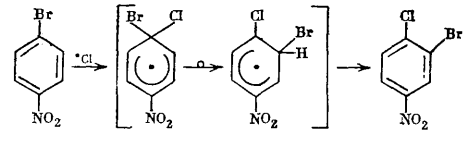


In his analysis of the work of Belgian chemists[79] on the photobromination of dihalogenobenzenes, Traynham[78] drew attention to the fact that 1,2,3-trihalogenobenzenes constitute an appreciable proportion of all the isomeric trihalogenobenzenes formed. He suggested that radical unco-σ-complexes are formed and that the halogen undergoes 1,2-migration in these σ-complexes:



The Belgian scientists, who did not agree with this interpretation of their results, carried out a thorough investigation of the isomeric composition of the products of the photobromination of *o*- and *m*-dihalogenbenzenes.[80] They showed that the reaction products contain only 3-bromo-1,2-dichlorobenzene (reaction of *o*-dichlorobenzene) and 2-bromo-1,3-dichlorobenzene (reaction of *m*-dichlorobenzene). However, the formation of these products fits within Traynham's scheme, while the absence of other isomeric 1,2,3-trihalogenobenzenes can be accounted for by the different capacities for migration of chlorine and bromine atoms (Br > Cl).

Yet another process in which the 1,2-migration of the halogen in cyclohexadienyl radicals has been demonstrated is the free-radical chlorination of *p*-halogenonitrobenzenes:[81,82]



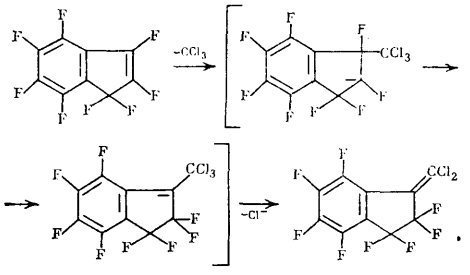
The structure of the rearranged product of this reaction also indicates the greater ease of the 1,2-migration of a bromine atom compared with a chlorine atom.

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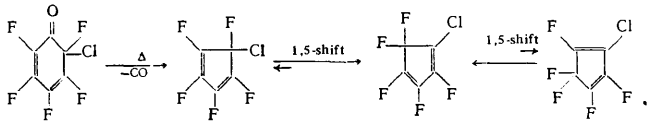
Thus analysis of the literature data shows that, whereas the migrations of a fluorine atom in neutral compounds are fairly common reactions and are consistent with modern theoretical views, the shifts of a fluorine atom in the intermediate species proceed via a fairly high energy barrier and require further theoretical consideration.

Most data available for the migration of a fluorine atom in intermediate species concern migrations in free radicals and, in particular, the 1,2-shift of a fluorine atom in cyclohexadienyl radicals. However, hitherto it is impossible to distinguish all the factors influencing the direction and energetics of the process. Presumably the energy of the 1,2-migration of a fluorine atom in radicals is intermediate between those of the 1,2-migrations in cations and anions. Although there is no experimental proof in the literature of the occurrence of the 1,2-shift of a fluorine atom in cations, Burdon and Parsons[61] believe that the 1,2-shift of a fluorine

atom in arenium ions is possible. Calculation by the CNDO/2 method of the relative energies of the isomeric arenium ions has shown that the stage involving the 1,2-shift of a fluorine atom is exothermic, but such a rearrangement should take place via a high energy barrier. It is believed that[61] it is achievable in the temperature range 200–500 °C. As regards the 1,2-shift of a fluorine atom in anions, the latter can apparently take place via a lower energy barrier than in the case of radicals and cations. Admittedly, in the latter case the interpretation of experimental data is hindered by the ease of abstraction of a fluoride ion from the anions. Nevertheless, for certain isomerisations proceeding with participation of anions, it is possible to postulate an intramolecular mechanism. For example, the formation of 1-dichloromethyleneperfluoroindan on interaction of perfluoroindene with sodium trichloroacetate can be represented as the result of isomerisation with formal 1,2-migration of a fluorine atom in the intermediate anion, although one cannot rule out pathways via the consecutive abstraction and addition of the fluoride anion:[83]



During the preparation of the manuscript for publication, several studies concerning the migration of a fluorine atom appeared in the literature. Thus the thermal 1,5-shift of a fluorine atom has been invoked[84] to account for the isomeric composition of the chloropentafluorocyclohexadienes formed on thermolysis of chloropentafluorocyclohexadienone:



Mal'tsev et al.[85] studied the isomerisation of bis(trifluoromethyl)carbene to perfluoropropene. The initial carbene was detected by IR spectroscopy in an argon matrix at 12–40 K:

$$(CF_3)_2C: \xrightarrow[\text{1,2-shift}]{} CF_3CF{=}CF_2 .$$

A study of the 1,2-migration of a fluorine atom in the 1,1,2-trifluoroethyl radical has been published recently.[86] The authors used the method proposed previously,[62] which consists in the addition of tritium atoms to fluorinated olefins:

$$CF_2{=}CHF \xrightarrow{T^{\cdot}} \dot{C}F_2{-}CHFT \xrightarrow{\circ} CF_3{-}\dot{C}HT \xrightarrow[-[F^{\cdot}]]{} CF_2{=}CHT .$$

Kotaka and Sato[86] explained by the 1,2-migration of a fluorine atom in the 1,1,2-trifluoroethyl radical the results of an earlier study[87] in which the formation of $CF_3CH_2CH_2CF_3$ was observed when a hydrogen atom was added to trifluoroethylene. Scott and Jennings[87] discussed the results of a calculation by the INDO method of the activation energies for the 1,2-migration of fluorine and hydrogen atoms in the radicals $\dot{C}F_2$–CHFT and $\dot{C}$FH–CFHT and suggested that in the excited radicals the 1,2-migration of a fluorine atom and not a hydrogen atom is energetically more favourable.

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Steric Structuring of Polyolefins by Chemical Methods

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The present state of the problem of the steric structuring of polyolefins by chemical cross-linking agents (organic peroxides, azo-compounds, and organo-silanes) is examined. The structure formation mechanisms, the process conditions, the requirements which must be met by cross-linking agents, the factors determining the properties of cross-linked polymers, as well as the prospects for the development of the method are discussed.
The bibliography includes 28 references.

CONTENTS

I. Introduction 72
II. The mechanism and kinetics of the cross-linking of polyolefins by chemical methods 72
III. The requirements which must be met by cross-linking agents 76
IV. The conditions in the structure formation processes 77
V. The constitution and properties of compositions undergoing cross linking 77
VI. Conclusion 80

I. INTRODUCTION

The steric structuring (cross-linking) of polyolefins is one of the principal ways of modifying their structure, which makes it possible to improve their operating characteristics and to extend the temperature range and types of applications of polyolefins.

Steric structuring is achieved by different methods: by radiation or ultraviolet light or with the aid of chemical cross-linking agents. The radiation structuring method does not as a rule require the introduction of special additives into the polymer. However, its application requires cumbersome and expensive apparatus and the maintenance of safety conditions. At the present time chemical structure formation is the commonest and most convenient procedure in practice and is employed in two principal versions: (1) the cross-linking of polyolefins with the aid of radical-forming agents (peroxides and azo-compounds) and (2) the cross-linking of polyolefins by organosilanes. The structuring of polyolefins by peroxides has been known for a long time. Organosilanes began to be used for this purpose more than 10 years ago, while azo-compounds have been applied only in recent years.

Despite the evident advances in the industrial use of chemical structuring, the theoretical aspects of the problem, in particular, the kinetics and mechanism of the process have not as yet been duly developed. The point is that the cross-linking reaction of polyolefins occurs either in the solid polymer or in its melt. It is known[1] that the structural-physical state is the most important factor influencing the chemical process in polymers. Structural microinhomogeneity of polymers is due to the inhomogeneity of the distribution of additives and reactants in the polymer system, the spatial localisation of the physical processes and chemical reactions in certain regions of the polymer, and also the dependence of the kinetic parameters on the kinetics of the molecular motions and molecular-relaxation properties of the polymer.[1] However, the kinetics and mechanisms of chemical structuring have so far been scarcely investigated from these standpoints.

There are extensive literature data concerning the structures and properties of cross-linked polyolefins, their relation with the initial compositions, and the determination of the kinetic parameters for the decomposition of peroxides and for the structure formation process. However, a considerable proportion of the results are unsuitable for the analysis of the state of the problem.

II. THE MECHANISM AND KINETICS OF THE CROSS-LINKING OF POLYOLEFINS BY CHEMICAL METHODS

The mechanism of cross-linking by radical forming agents has been investigated only in relation to organic peroxides. According to existing ideas,[2] it includes radical formation by the homolytic decomposition of the peroxide, the transfer of the radical activity to the polyolefin macromolecule by the abstraction of a hydrogen atom from the latter, and the recombination of the polyolefin macroradicals with formation of carbon–carbon cross-links:

$$I \xrightarrow{k_1} 2\dot{R}\,, \tag{1}$$

$$\dot{R} + PH \xrightarrow{k_2} \dot{P} + RH\,, \tag{2}$$

$$\dot{P} + \dot{P} \xrightarrow{k_3} P{-}P\,, \tag{3}$$

Apart from the three main elementary reactions, there is a possibility of the occurrence of radical side reactions, for example, the radical-induced decomposition of the peroxide, the fragmentation of the macroradicals, their interaction with low-molecular-weight radicals, disproportionation, etc.:

$$\dot{R} + I \xrightarrow{k_4} \dot{R}' + R\sim\,, \tag{4}$$

$$\dot{P} + I \xrightarrow{k_4} \dot{R}' + P\sim\,, \tag{5}$$

$$\dot{P} \xrightarrow{k_6} P_{=} + \dot{P}'\,, \tag{6}$$

$$\dot{P} + \dot{P} \xrightarrow{k_3'} \text{products of disproportionation of macroradicals,}$$

$$\left.\begin{aligned} \dot{P} + \dot{R} &\xrightarrow{k_7} \\ \dot{R} + \dot{R} &\xrightarrow{k_8} \end{aligned}\right\} \text{products of the recombination and disproportionation of radicals,} \tag{7, 8}$$

where $P_{=}$ is a macromolecule with a double bond.

The rate-limiting stages of the cross-linking process are the consecutive reactions (1) and (2). Part of the peroxide, decomposing via a mechanism other than the unimolecular mechanism, is effectively lost as regards the structuring process.[3] The presence or absence of the induced decomposition is determined by the nature of the cross-linking agent, other conditions being equal.

From the standpoint of the final result, two elementary reactions are decisive: the recombination reaction (3) and the degradation reaction (6) of the polymer radicals. Depending on the structure of the polymer radicals, reaction (3) leads to linear growth, branching, or cross-linking of the macromolecule; reaction (6) entails degradation. The preferential occurrence of each of these reactions depends to a large extent on the efficiency of the steric structuring process, i.e. on the number of cross-links arising in the polymer as a result of the decomposition of one peroxide group. For example, in polyethylene the polymer radicals almost always recombine with formation of cross-links. Polymers containing tertiary carbon atoms tend to undergo degradation.

The study of the transformations occurring on decomposition of benzoyl peroxide in polyethylene, polypropylene, and polyisobutylene made it possible to derive general kinetic equations, which take into account the possibility of the simultaneous occurrence of the structuring and degradation reactions in polyolefins.[4]

1. For the unimolecular decomposition of the peroxide [reaction (1)]:

$$\Delta n = K_s[I]_0(1 - e^{-k_1 t})/k_1 - K_d\{[I]_0(1 - e^{-k_1 t})/k_1\}^{1/2} .$$

2. For the chain composition of the peroxide [reaction (4)]:

$$\Delta n = K_s \frac{2.303 \lg \{e^{k_1 t}(k_c[I]_0/k_1 + 1) - k_c[I]_0/k_1\} - k_1 t}{k_c} - K_d\left\{\frac{2.303 \lg \{e^{k_1 t}(k_c[I]_0/k_1 + 1) - k_c[I]_0/k_1\} - k_1 t}{k_c}\right\}^{1/2} .$$

3. For the chain decomposition of the peroxide [reaction (5)]:

$$\Delta n = K_s \frac{2k_1}{k_c^2}\left[(a+1) - \frac{A(a+1)}{A(a+1)-a} - 2.303 \lg \frac{A(a+1)-a}{A}\right] - K_d\left\{\frac{2k_1}{k_c^2}\left[(a+1) - \frac{A(a+1)}{A(a+1)-a} - 2.303 \lg \frac{A(a+1)-a}{A}\right]\right\}^{1/2} ,$$

where Δn is the change in the concentration of bonds in the polymer, $K_S = k_1 k_3/(k_3 + k'_3)$ the structuring constant,

$$K_c = k_1^{1/2} k_6/(k_3 + k'_3)^{1/2}$$

the degradation constant, k_c the rate constant for the chain decomposition of the peroxide, $[I]_0$ the initial peroxide concentration, t the time, $a = k_c[I]_0^{1/2}/k_1$, and $A = e^{k_1 t/2}$.

The equations take into account, on the one hand, the possibility of both the unimolecular and chain decomposition of the peroxide and, on the other, various types of radical termination. However, these equations are nevertheless specific in character and, like the mechanism presented above [reactions (1)–(8)], did not take into account the structural-physical characteristics of the polymer, its molecular weight distribution, and the role of the cage effect in the system and of the delay transfer in the transport of the reacting species—radicals and molecules. The necessity to take these factors into account is indicated by experimental data. For example, the rate of radical reactions in low density polyethylene (LDPE) is higher by two orders of magnitude than in high density polyethylene (HDPE).[5] The introduction of identical amounts of the cross-linking agent, other conditions being equal, leads to the formation of a larger number of cross-links in HDPE than in LDPE (Fig. 1).[6]

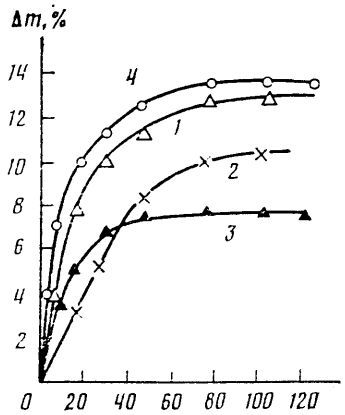


Figure 1. Kinetic curves for the swelling (at 140 °C) in *p*-xylene of HDPE (curves *1*–*3*) and LDPE (curve *4*) specimens cross-linked by di-t-butylperoxyisopropylbenzene. The content of peroxide (%): 1) 1.5; 2) and 4) 2.0; 3) 3.0.

Table 1. The efficiency of the cross linking of linear polyethylene (d = 0.960 g cm^{-3}) by dicumenyl peroxide at the initial gel formation point (at 150 °C).[7]

Polymer	$10^{-3}M_w$	M_w/M_n	c^{**}, mmol kg^{-1}		Efficiency of cross linking***, %
			experiment	calculation	
1	79.0	9.0	42	12.6	30
2	70.0	10.0	50	14.3	29
3	81.0	12.5	55	12.3	22
4	61.0	5.0	63	16.4	26
5	60.0	4.0	66	16.7	25
6	40.0	5.0	77	25.0	32
7	58.0	8.0	68	17.3	25
8	60.0	6.0	70	16.7	24
9	95.0	3.0	33	10.5	32
10	49.5	2.7	70	20.0	29
C	60.0	3.5	22	16.7	76
H	52.0	6.0	81	19.3	24

*Polymers 1–10 contain less than 0.07 of a vinyl group per 1000 carbon atoms. The mixture of polymer 10 with dicumenyl peroxide was freed from oxygen in an atmosphere of nitrogen before the reaction. Polymer C contains 0.5 of a vinyl group per 1000 carbon atoms and H represents the hydrogenated polymer.

**Here c is the concentration of dicumenyloxy-radicals.

***The ratio of the calculated and real peroxide concentrations at the beginning of gel formation.

The study of the characteristic features of the cross linking of linear polyethylene[7] in the presence of dicumenyl peroxide showed that the efficiency of cross linking, the yield of the product of the thermolysis of the peroxide, and the preferential occurrence of one of the competing reactions are

significantly influenced by the presence of a vinyl group in the system, whose carriers may be both the peroxide decomposition products and the polyolefin. This is expressed, in particular, by the considerable discrepancy between the theoretical amount of cumenyloxy-radicals, calculated from the Flory–Stockmayer relation, and its experimental amount ensuring the same efficiency of cross linking[7] (Table 1). The kinetic parameters of the cross linking by peroxides depend on the concentration of active oxygen in the system, the nature and concentrations of the components, and the process temperature (Fig.2).[6] Furthermore, the rate of cross linking and the yield of the cross-linked polymer are influenced by the pressure;[8] it may be that the observed effect is caused by the decrease in the activation volume of the reaction.[9]

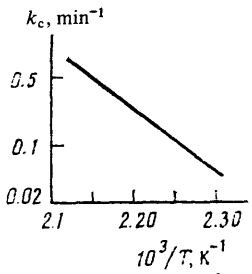


Figure 2. Temperature dependence of the rate constant for the cross linking of polyethylene with the density $d = 0.960$ g cm^{-3}.[6]

The examples considered clearly indicate the imperfection of the existing ideas about the mechanism of the cross linking of polyolefins by organic peroxides, as they fail to take into account a whole series of significant factors.

The cross linking of polyolefins by azo-compounds has been studied still less. It has been assumed for a long time[10] that azo-compounds cannot serve as initiators of the cross linking of polyolefins, because the radicals formed on decomposition of the majority of them [via reaction (1)] are incapable of abstracting hydrogen from the polyolefin macromolecule. However, when the polymer system contains double bonds (ethylene–propene–diene copolymers, their mixtures with saturated polyolefins, etc.), structuring can occur as a result of the addition of primary radicals with dissociation of double bonds according to the mechanism[10]

$$R + CH_2{=}CH{-}R'{-}CH{=}CH_2 \rightarrow R{-}CH_2{-}\dot{C}H{-}R'{-}CH{=}CH_2 ,$$

$$R{-}CH_2{-}\dot{C}H{-}R'{-}CH{=}CH_2 + PH \rightarrow R{-}CH_2{-}CH_2{-}R'{-}CH{=}CH_2 + \dot{P} ,$$

$$R{-}CH_2{-}CH{-}R'{-}\dot{C}H{=}CH_2 + P \rightarrow R{-}CH_2{-}\underset{\displaystyle P}{CH}{-}R'{-}CH{=}CH_2 ,$$

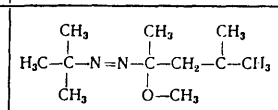
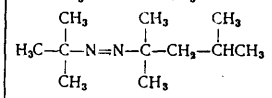
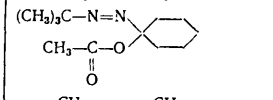
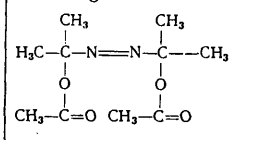
$$R{-}CH_2{-}\underset{\displaystyle P}{CH}{-}R'{-}CH{=}CH_2 + \dot{R} \rightarrow R{-}CH_2{-}\underset{\displaystyle P}{CH}{-}R'{-}CH{-}CH_2{-}R ,$$

$$R{-}CH_2{-}\underset{\displaystyle P}{CH}{-}R'{-}\dot{C}H{-}CH_2{-}R + P \rightarrow R{-}CH_2{-}\underset{\displaystyle P}{CH}{-}R'{-}\underset{\displaystyle P}{C}{-}CH_2R .$$

Thorough investigation of the mechanism is still to come, but it is already clear that the use of azo-compounds makes it possible to avoid degradation [reaction (6)] in the structuring of polyolefins containing tertiary carbon atoms. Furthermore, additional possibilities arise for increasing the efficiency of the action of the cross-linking agent as a result of the use of mixtures of azo-compounds, or regulating the duration and extent of the structuring process, etc.[10] Table 2 presents certain azo-compounds recommended for the cross-linking of polyolefins.

Whilst having a series of undoubted advantages, which include high strength of the finished article, resistance to cracking and the action of organic solvents and mechanical stresses at high temperatures, the possibility of varying its properties over a wide range, the uniformity of its structuring throughout its volume, etc., cross linking by radical forming compounds also suffers from significant disadvantages. In the first place, one should note the possibility of the premature cross linking of the material already in the stage where the cross-linking agent is introduced into the polymer. Another disadvantage is the limited choice of methods suitable for the preparation of the finished articles and the compositions undergoing cross linking. The use of organosilanes as cross-linking agents makes it possible to eliminate some of these disadvantages and provides a fundamentally new solution to the problem.

Table 2. Azo-compound cross-linking agents.[10]

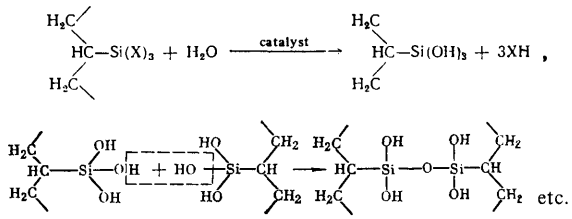
Name		Formula	Temperature, °C	
chemical	commercial		τ = 10 h	τ = 12 h
2-t-Butylazo-2-methoxy-4-methylpentane	Luazo-135		135	155
2-t-Butylazo-2,4-dimethylpentane	Luazo-148		148	168
1-t-Butylazo-1-acetoxycyclohexane	Luazo-165		165	187
2,2-Azobis-2-acetoxypropane	Luazo AP		189	215

Notation: τ is the decomposition half-life of the azo-compound.

The mechanism of the cross linking pf polyolefins by organosilanes has been described in the literature in the most general form and we are unaware of any far reaching studies on the process kinetics. According to the available data, the cross linking of the polyolefins includes two main reactions: the grafting of the organosilane of the type $R_nSIX_{(4-n)}$ to the polyolefin and subsequent structuring of the modified polymer in the presence of water and a hydrolysis catalyst[11] [X = hydrogen, a halogen, or a radical (alkyl, aryl, arylalkyl, cycloalkyl, alkylamine, arylamine, etc.); R = radicals with olefinic double bonds containing 2–12 carbon atoms; n = 1, 2]. It has been suggested[12] that the grafting of the silane to the polyolefin can be represented as follows in a general form:

$$\sim CH_2{-}CH_2{-}CH_2 \sim + RSi(X)_3 \rightarrow \sim CH_2{-}\underset{\displaystyle Si(X)_3}{\overset{\displaystyle H}{C}}{-}CH_2 \sim ,$$

and the second stage can be represented schematically by



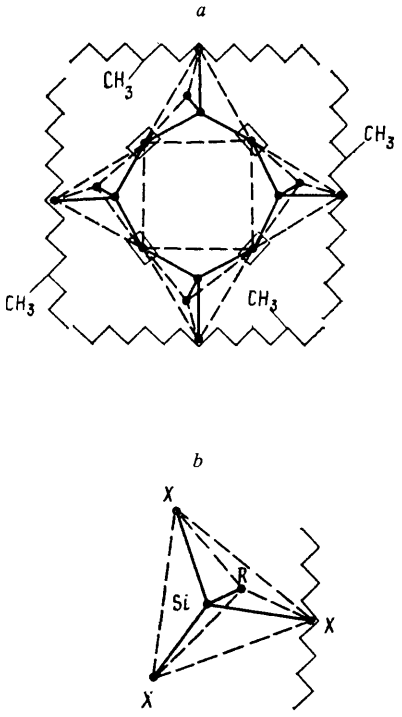


Figure 3. The configuration of the cross-linking nodes: *a*) the node linking four macromolecules, the centres of the intermolecular interaction of the silane substituent being indicated by rectangles; *b*) schematic illustration of the position of substituents capable of participating in the cross-linking process.

A polyolefine modified by silane is a polyfunctional compound which constitutes a kind of cross-linking centre capable of binding several macromolecules at once. Under these conditions, the four substituents in the silane molecule capable of being joined to macromolecules and to one another form a tetrahedron with the silicon atom at the centre (Fig.3*b*).[13] In the polymer there are usually three reactive substituents. However, as can be seen from Fig.3*a*, on average only two substituents are involved in the structuring process. Structuring by silanes results in the formation of polymers whose properties differ from those of polyolefins cross-linked by organic peroxides, which is caused to a large extent by the difference in the nature of the cross-link (–Si–O–Si–C instead of –C–C–) and in the functionality of the nodes of the network.[13]

The silane is usually grafted to the polyolefin by the mechanochemical degradation method using one of the familiar procedures for the processing of polymers. The best results have been obtained in a Banbury blender and on a rolling machine.[12] The conditions in the mechanical treatment depend on the type of polymer, its molecular weight, the required degree of grafting, and the type of equipment.[11] The efficiency of the grafting process can be increased by introducing into the polymer substances capable of generating free radicals (peroxides and azo-compounds). The content of the radical forming compound is determined by the type of polyolefin and the required degree of grafting, but it should not be so large that the polymer is cross-linked.

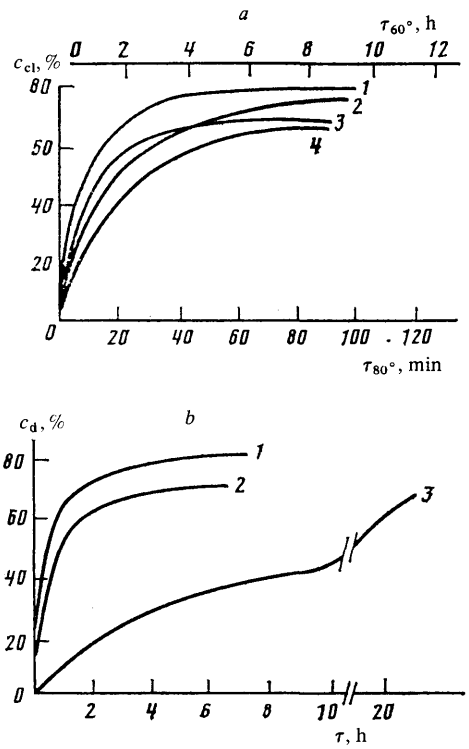
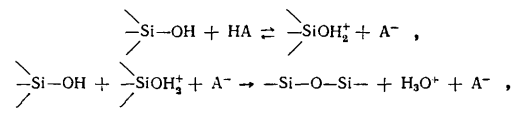


Figure 4. Dependence of the content of the cross linked-fraction c_{cl} in the composition on the structuring process conditions: *a*) Moldex S-181 in water: 1) at 80 °C; 2) at 60 °C; 3) and 4) Moldex S-161 under analogous conditions [$\tau_{60°}$ (h) and $\tau_{80°}$ (min) are the times during which the compositions are kept in water at 60° and 80 °C]; *b*: 1) Moldex S-181 at 40 °C and 90% humidity; 2) Moldex S-161 under the same conditions; 3) Moldex S-161 at 25 °C [τ is the exposure time (h)].[12]

The polymer modified with a silane is hydrolysed by atmospheric moisture even at room temperature. Nevertheless, in order to accelerate the reaction, the cross linking is frequently carried out in an aqueous medium at 40–90 °C in the presence of a catalyst or by treatment with water vapour at a temperature ≥100 °C. The limiting cross-linking density achieved under these conditions does not then change (Fig.4). The hydrolysis catalysts can be inorganic

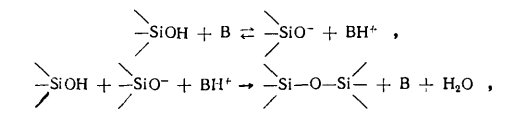
and aliphatic acids, organic bases (ethylamine, dibutylamine, and piperidine), orthotitanate esters, chelates, and metal carboxylates. Depending on the nature of the catalyst, the following mechanisms have been proposed for the formation of the siloxane linkage:[12]

(a) in the presence of acids:



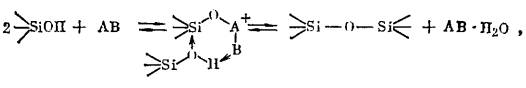
where A is the acid anion;

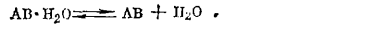
(b) in the presence of alkali:



where B is the base;

(c) in the presence of neutral salts:





Among the multiplicity of catalysts for cross linking by organosilanes, preference is given to organotin compounds such as dibutyltin dilaurate, dibutyltin diacetate, and dibutyltin dioctanate. These compounds are neutral salts, exhibit a high catalytic activity, and do not generate a corrosive medium.[11,12]

The grafting and structuring stages can be combined by introducing into the system additives forming water in the course of their chemical interaction with the components of the system.[12] Polyolefins with any density and any parameters of the fluidity of the melt can be subjected to structuring by organosilanes.

III. THE REQUIRMENTS WHICH MUST BE MET BY CROSS-LINKING AGENTS

The essential requirements which must be satisfied by the agents for the cross linking of polyolefins are determined primarily by the mechanism of the cross-linking process, its kinetic features, and the way in which it is achieved. Furthermore, there exist a series of technical and economic requirements, common to all types of chemical cross-linking agents: stability and low volatility under the conditions where they are combined with the polymer, volatility and lack of toxicity of the thermolysis products or the products of the interaction with the components of the composition, and ready availability of the raw material; for radical forming agents, a high rate of decomposition (decomposition half-life 4–6 min) at a temperature exceeding by 40–60 °C the temperature at which they are introduced into the polymer is sufficient.

Reactions (1) and (2) determine the principal requirement which must be met by peroxides as cross-linking agents: the ability to generate radicals which are sufficiently active in reactions involving the abstraction of hydrogen from the polymer chain. It is known that the activity of radicals in hydrogen abstraction reactions depends both on their intrinsic structure and on the structure of the elements of the macrochain.[7,8] In the cross-linking reactions of polyolefins, it is preferable to use peroxides generating alkoxy-radicals on decomposition. The study of the behaviour of a series of asymmetric peroxides of the type R–O–O–R′ in a cross-linking process showed that t-butyl cumenyl peroxide exhibits the maximum efficiency. Its decomposition results in the formation of t-butoxy- and cumenyloxy-radicals, which decompose in their turn to methyl radicals and correspondingly to acetone and acetophenone.

Among peroxides with different structures—peracids, peracetals, perketals, peresters, hydroperoxides, and dialkyl and diacyl peroxides—tertiary dialkyl peroxides satisfy most fully the requirement specified. The optimum conditions for the technological cross-linking process and the optimum characteristics of the cross-linked polyolefins are ensured by dicumenyl peroxide, which is widely used on an industrial scale. The mechanism and kinetics of its thermal decomposition have been studied in fair detail.[14] The formation of the highly toxic actophenone in the thermolysis of dicumenyl peroxide has led to the search for other peroxides combining all the positive qualities of dicumenyl peroxide with the absence of toxic decomposition products. Such cross-linking agents proved to be certain bifunctional peroxides. The recommended temperatures of their mixing with the polymer (T_{mix}) and the cross linking temperatures (T_{cl}) as well as the efficiencies (f) of the cross linking of LDPE are indicated below:[15]

	T_{mix}, °C	T_{cl}, °C	f
Di-t-butyl peroxide	up to 100	150	–
Dicumenyl peroxide	up to 120	160	0.61
1,3-Di-t-butylperoxyisopropylbenzene	up to 130	170	–
1,4-Di-t-butylperoxyisopropylbenzene	up to 130	170	–
n-Butyl-4,4′-di-t-butylperoxyvalerate	up to 110	150	–
1,1-Di-t-butylperoxy-3,3,5-trimethylcyclo hexane	up to 100	140	–
2,5-Di-t-butylperoxy-2,5-dimethylhexane	up to 130	170	0.29
2,5-Di-t-butylperoxy-2,5-dimethylhex-3-yne	up to 130	170	0.74

The possibility of the cross linking of polyolefins by two-component cross-linking systems generating radicals in the course of the oxidation-reduction reaction is of definite interest. The cross-linking system consisting of a hydroperoxide and a variable valence metal ion may serve as an example.[16] The low activation energy for the interaction of the hydroperoxide with a variable valence metal ion makes it possible to carry out the structuring process at lower temperatures and to avoid the premature cross linking of the polymer. The rate of the process can be regulated by varying not only the temperature but also the content of the metal. The advantage of such systems, consisting in lowering the temperature of the cross linking process, proved at the same time to be their disadvantage, since they can initiate structuring only during the preparation and formation of the mixtures. However, this principle of the formation of macroradicals ensures contact between the components via diffusion at the required stages of the process. When it is applied to the preparation of thin-layer materials, the cross-linking temperature is appreciably reduced, which makes it possible to cross-link polyethylene films at temperatures which do not induce their deformation.

The *meta*- and *para*-isomers of di-t-butylperoxyisopropylbenzene or their mixture (peroxymon) have come to be most widely used. The diperoxy-derivatives of ketones and tri- and tetra-peroxides of different structure can be used as cross-linking agents.[17] However, the methods of their synthesis are as a rule complex, the raw materials are difficult to obtain, and the polyolefins cross-linked by them do not manifest any significant advantages in their properties. For this reason, the above group of peroxides can be of interest only for the investigation of the influence of the

structure and functionality of the peroxide on the mechanism and kinetics of the cross-linking process. The hypothesis that the bifunctional di-t-butylperoxyisopropylbenzene can be more efficient in the cross linking of polyolefins than dicumenyl peroxide has not been confirmed experimentally.[18]

Subsequently it was shown[19] that there is a possibility of the stepwise decomposition of peroxy-groups in diperoxides. The activation energy for the decomposition of the second peroxy-group is greater (E_1 = 152 kJ mol^{-1}, E_2 = 161 kJ mol^{-1}) and the rate of decomposition is lower—$k^1_{decomp} = 58 \times 10^{-5}$ s^{-1} and $k^2_{decomp} = 30 \times 10^{-5}$ s^{-1} at 150 °C (for comparison, we may recall that the values determined under analogous conditions for dicumenyl peroxide are E = 153 kJ mol^{-1} and $k_{decomp} = 53 \times 10^{-5}$ s^{-1}).[19] The observed features are due to the differences in the structures of the peroxide complexes and in the stability of the radicals formed on decomposition of the first and second peroxy-groups.[19] These differences cause the reduced efficiency of the cross linking of polyolefines in the presence of di-t-butylperoxyisopropylbenzene compared with dicumenyl peroxide in the temperature range 140–160 °C. An increase in temperature reduces the difference.

It had been postulated earlier that the mechanism of the thermal decomposition of peroxides remains unchanged on passing from model systems to the polymer.[20] However, in the light of the existing ideas about the mechanisms of solid-phase reactions,[1] this hypothesis must be regarded as erroneous and as associated with the low accuracy of the experiment.

Specific requirements which must be met by cross-linking agents are closely related to the problem of the introduction and decomposition of radical-forming compounds in polyolefins.

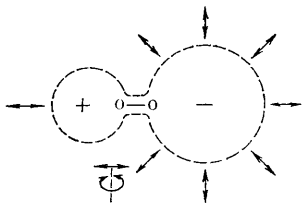
IV. THE CONDITIONS IN THE STRUCTURE FORMATION PROCESSES

Radical-forming cross-linking agents can be introduced into polyolefins by different methods: (1) by stirring into a polymer melt, (2) by the diffusion method, (3) by dry mixing, and (4) by the internal synthesis of the cross-linking agent.[21] As an example of the use of the last method, one may quote the synthesis of di-t-butyl peroxalate from tetraalkyl hydroperoxide and oxalyl chloride directly in the bulk of the polymer.[23]

Silanes can be introduced into the polymer melt or can be dispersed on the surface of the polyolefin. Hydrolysis catalysts are introduced into the composition in different ways: before the start of the reaction involving the grafting of the silane to the polyolefin, during this reaction, or after it has been completed; by mixing the components; by diffusion; by treating the grafted copolymer with an aqueous suspension, emulsion, or solution of the catalyst.[11]

Until recently, only thermolysis has been used to decompose the peroxide into the free radicals. The application for this purpose of an ultrahigh frequency electromagnetic field (microwave mixing or, what amounts to the same thing, UHF mixing, UHF cross linking) has opened up new possibilities.[22] Cross linking by exposure to a UHF field can be achieved in three ways.

1. Decomposition in the UHF field of peroxides, for example, t-butyl peroxybenzoate or di-t-butyl peroxyterephthalate. The peroxide decomposes as a consequence of the instantaneous absorption of energy from the UHF field, usually at a frequency of 2450 MHz, in accordance with the scheme



2. The use of weakly polar peroxides and auxiliary substances highly active in a UHF field, such as halogenohydrocarbons, carbon black, triallyloxy-*s*-triazine, etc. The molecules of the auxiliary substances absorb the energy of the UHF field and transmit it to the peroxide molecules. The polymer composition being cross linked in the UHF field is heated uniformly to the temperature at which the thermal composition of the peroxide begins.[21]

3. The use of auxiliary substances highly active in a UHF field and of weakly polar products forming complexes with them. As a result, the peroxide molecules are always in the immediate vicinity of the molecules of the auxiliary substances which transmit to them the absorbed energy from the UHF field, so that the thermolysis of the peroxide is possible at a lower temperature of the polymer.

There is as yet little information in the literature about the mechanism of the microwave cross linking, the decomposition of peroxides in a UHF field, and the effect of auxiliary additives, the kinetic process parameters, etc. Only the influence of the nature of the peroxide and of the auxiliary additives on their activity in the UHF field and on the degree of structuring of the polyethylene has been noted and the dependence of the rate of cross linking on the concentration of the peroxide, the initial temperature of the polymer composition, and the duration of the action of the UHF field has also been observed.[22,23] Nevertheless, the advantages of the method of the microwave cross linking of polyolefins are already evident: the decreased energy requirement for the process, the decrease in the length of the industrial production line and of the cooling zone, and the possibility of cross linking a thick-walled article. Furthermore, the decomposition of polar peroxides to weakly polar products has a favourable effect on the dielectric characteristics of the structured polymers (when di-t-butyl peroxyterephthalate is used for polyethylene, the tangent of the dielectric loss angle tan $\delta = 1.5 \times 10^{-4}$ at 20 °C and a frequency of 100 Hz, while the dielectric constant is ε = 2.34).[22] The possibility of cross linking articles regardless of their thickness is the main advantage of the method and is responsible for its vigorous development and industrial application.[22]

V. THE CONSTITUTION AND PROPERTIES OF COMPOSITIONS UNDERGOING CROSS LINKING

The influence of the constitution of the compositions undergoing cross linking on their properties can be examined fully enough only in relation to polyolefins structured by organic peroxides, since these have been most thoroughly investigated.

A real composition undergoing cross linking is a complex polymer system, which contains as a rule stabilisers, accelerators, fillers, and modifying agents which are not always inert towards the cross-linking agents or free radicals. The antioxidant preventing degradation is an obligatory component of cross-linking compositions based on polyolefins. The structuring and inhibited thermal oxidation reactions

proceed via a radical mechanism, so that, when the polymer contains simultaneously a peroxide and an antioxidant, the latter interacts with the radicals formed on decomposition of the cross-linking agent. The reaction products inhibit the cross-linking reaction and reduce the efficiency of the structuring process. Apart from reactions (1)–(8), there is then a possibility of the occurrence of the following elementary reactions:[20]

$$\dot{R} + YH \xrightarrow{k_9} \dot{X} + RH \qquad (9)$$

$$\left.\begin{aligned} \dot{Y} + \dot{Y} &\xrightarrow{k_{10}} \\ \dot{P} + \dot{Y} &\xrightarrow{k_{11}} \end{aligned}\right\} \text{reaction products.} \qquad (10),\ (11)$$

For the steric structuring by peroxides, the relative reactivity of the antioxidant can be estimated with the aid of the relation (Fig.5):[20]

$$\left(\frac{[i]}{[i']}\right)^{1/2} = rk\frac{[YH]}{[PH]} + k$$

where [YH] and [PH] are the amounts of the antioxidant in the polymer (moles), k is the ratio of the rate constants characterising the cross-linking reactions of the stabilised and unstabilised polyolefins, r is the relative reactivity of the antioxidant, and [i] is the amount of peroxide which induces the formation of the same number of cross-links in the unstabilised polyolefins as the amount [i'] in the stabilised polyolefin.

Thus the relative reactivity of the antioxidant can be estimated from the ratio of [i] and [i']. The reactivity of antioxidants of the phenolic type is higher than that of antioxidants of the amine type. The values of r and k for the polyethylene–dicumenyl peroxide system are presented below; the data obtained using 1,3-di-t-butylperoxyisopropylbenzene are indicated in brackets:[23]

	r	k
N-Cyclohexyl-*N*-phenyl-*p*-phenylenediamine	60	1.02
NN'-Diphenyl-*p*-phenylenediamine	90	0.97
NN'-Dinaphthyl-*p*-phenylenediamine	160(280)	0.99(0.90)
2,2'-Methylenebis(6-t-butyl-4-methylphenol)	540(600)	0.91(0.86)
4,4'-Thiobis(6-t-butyl-3-methylphenol)	1500	0.83

In order to intensify the peroxide cross-linking process, one may introduce into the composition cross-linking coagents, whose role is usually fulfilled by sulphur or polyfunctional monomers [divinylbenzene, trialkyl cyanurate, tri(hydroxymethyl)propane trimethacrylate, pentaerythrityl tetramethacrylate].[2]

The introduction of a filler also influences the kinetic structuring parameters, since the rates of the elmentary reactions occurring on the filler surface and in the bulk of the polymer are different.[21] This difference is caused by the selective adsorption of the reactant at the interface and by the involvement in the reactions of the functional groups of the filler. The adsorption interaction of peroxides with the filler surface may be abolished by introducing additives (for example, poly-1,2-dihydro-2,2,4-trimethylquinoline) which are adsorbed first on the filler surface.

Fillers containing on their surfaces acid centres (carbon black, kaolin, etc.) induce an ineffective (non-radical) decomposition of the peroxide. This reduces the efficiency and density of the cross linking and the physicomechanical characteristics of the structured polymer are altered (Table 3).

Table 3. The physicomechanical characteristics of cross-linked filled LDPE (d = 0.917 g cm^{-3}, dimethyl peroxide content 2.5 wt.%).[17]

Filler	c_f, %	σ_b, MPa	l, %	$\Delta\Sigma$*, %
—	—	14.5	500	45.0
Chalk	10.0	12.0	350	30.0
Chalk	20.0	13.5	300	23.0
Talc	10.0	11.0	360	23.0
Kaolin	20.0	8.0	120	83.0
Kaolin	30.0	9.0	100	60.0

Notation: c_f is the content of the filler, σ_b the breaking stress on extension, l the relative elongation at rupture, and $\Delta\Sigma$ the deformation under a load of 5 N at 200 °C.

*The cross-linking density was estimated from the degree of deformation.

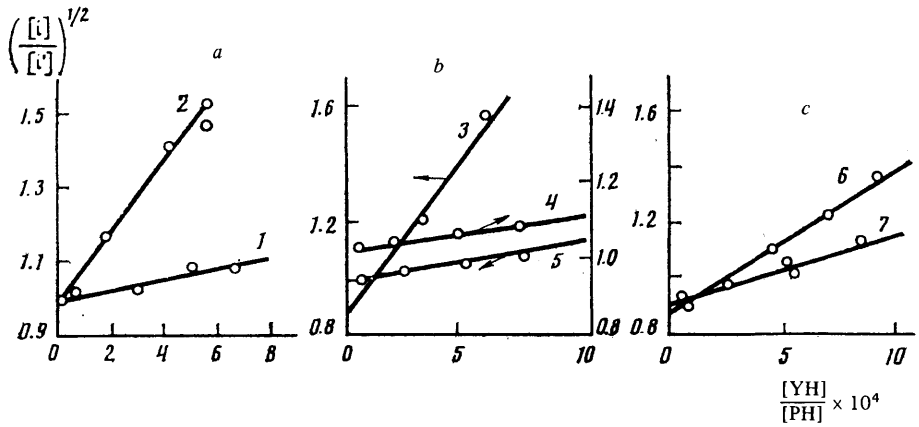


Figure 5. Dependence of $\{[i]/[i']\}^{1/2}$ on the antioxidant/polyethylene concentration ratio;[20] cross-linking agents: *a*) and *b*) dicumenyl peroxide; *c*) 1,3-di-t-butylperoxyisopropylbenzene; antioxidants: 1) and 7) *NN'*-dinaphthyl-*p*-phenylenediamine; 2) nickel dibutyldithiocarbamate; 3) 4,4'-thiobis(6-t-butyl-3-methylphenol); 4) *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine; 5) *NN'*-diphenyl-*p*-phenylenediamine; 6) 2,2'methylenebis(6-t-butyl-4-methylphenol).

The properties of cross-linked polyolefins are determined by a multiplicity of factors, the most important of which is the cross-linking parameter. In a number of studies, use has been made of the concept of the cross-linking density, which is either identical with the concept of the cross-linking parameter or is expressed as (a) the concentration of the effective chains, (b) the number of cross-linking sites referred to 1000 carbon atoms, and (c) the molecular weight of the section of the chain included between two nodes (M_C).[6,13]

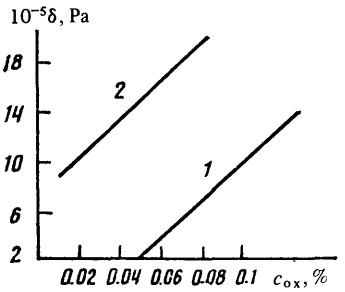


Figure 6. Dependence of the cross-linking density (estimated from the modulus of shear δ) of polyethylene with different densities on the content of active oxygen c_{ox} in the system: 1) d = 0.924 g cm^{-3}; 2) d = 0.960 g cm^{-3}.

The cross-linking parameter of polyolefins is determined by the process temperature, the concentration of active oxygen (Fig.6), the structural-morphological characteristics of the polymer, and the nature and concentration of other ingredients of the composition.[24] With increase in the cross-linking parameter, the relative elongation[24] and density of the polyolefins decrease (Fig.7) (according to Voight,[13] the relative elongation does not change) and their deformability by mechanical loads also diminishes (Fig.8). The content of the gel fraction changes little as the cross-linking density is varied (Fig.9). The point is that, even for low values of the latter, the extractable part of the polymer is small. Theoretically two cross-linking nodes per mass-average macromolecule are sufficient for the formation of an insoluble gel, but, depending on the molecular weight distribution (MWD) of the polyolefin, the content of the gel fraction may be different for the same cross-linking parameter.[25]

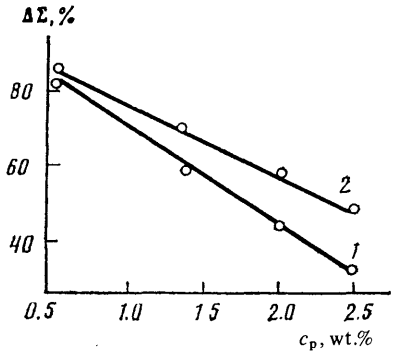


Figure 8. Dependence of the degree of deformation $\Delta\Sigma$ of cross-linked LDPE under a load of 5 N at 200 °C on the peroxide concentration c_p: 1) 2,5-di-t-butylperoxy-2,5-dimethylhexane; 2) 2,5-di-t-butylperoxy-2,5-dimethylhex-3-yne.

Since the main field where cross-linked compositions are used is the electrotechnical industry, it is necessary to know the factors determining their dielectric characteristics. These include the content, volatility, and polarity of the components of the polymer composition. An increase in polarity and a decrease in volatility impair the dielectric parameters.

The degree of crystallinity and the size of the unit cell of the cross-linked polyolefin are independent of the type and content of the peroxide.[26,27] Thus, whereas the degree of crystallinity is about 65% for LDPE (d = 0.917 g cm^{-3}), the value for the same polymer cross-linked in the melt by 2,5-di-t-butylperoxy-2,5-dimethylhexane or 2,5-di-t-butylperoxy-2,5-dimethylhex-3-yne is 33–37% for a peroxide concentration in the composition of 0.5–4.5%. The average size of the crystallites is 70 Å.[27] It is of interest to elucidate whether the structuring process occurs preferentially in the amorphous or crystalline phases of the polymer. So

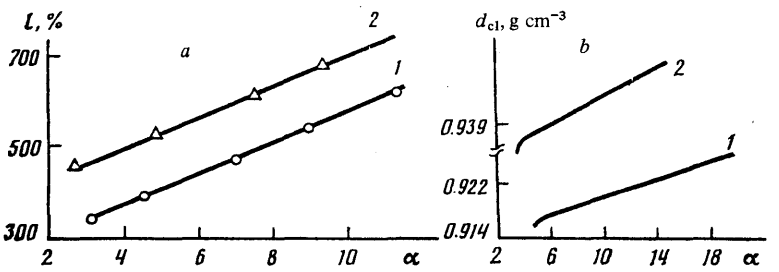


Figure 7. Dependence of the relative elongation l (a) and the cross-linking density d_{cl} (b) of cross-linked polyethylene with different densities [1) d = 0.924 g cm^{-3}; 2) d = 0.960 g cm^{-3}] on the swelling coefficient α determined at 140 °C.[6]

far there is no unanimous view concerning the character of the distribution of the cross-links between the phases of polyolefins. However, there is hardly any point in considering the probability of the occurrence of the structuring process in a particular phase[28] in those cases where it takes place in the polymer melt and the phase structure is established after the completion of the structuring process on cooling the specimen.

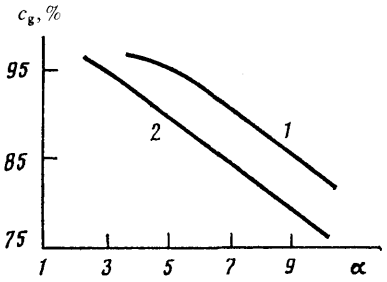


Figure 9. Dependence of the content of the gel fraction c_g in polyethylene with different densities on the swelling coefficient α:[6] 1) d = 0.960 g cm^{-3}; 2) d = 0.924 g cm^{-3}.

VI. CONCLUSION

We examined above the current state of the problem of the steric structuring of polyolefins by chemical methods. The questions of the technology, the specificity and importance of which require special consideration, were not considered.

At the present time, it is evident that the method of cross linking polyolefins or organic peroxides in the thermal decomposition of the latter occupies a leading position as regards its industrial application and practical value. It is also the method which is the most thoroughly investigated. The successive development and improvement of this method requires, firstly, the study of the mechanism of the thermal decomposition of organic peroxides in polyolefins and model hydrocarbons for the critical analysis of the mechanism adopted for the structuring process; secondly, the development and organisation of the industrial manufacture of effective new-generation structuring agents are needed. It is also useful to investigate the structuring effect of mixtures of organic peroxides as one method for increasing the efficiency of the process and for improving the technology.

From the standpoint of industrial application, the structuring of polyolefins by organic peroxides in the course of their decomposition by a UHF field is the most advanced application. The development of this application requires the study of the kinetics and mechanism of the microwave cross linking and the development and industrial application of polar peroxides.

The method of structuring polyolefins by organosilanes has a series of undoubted advantages, which has led to its vigorous industrial application (approximately 25 companies are engaged in this problem in Western Europe alone), despite the fact that it has been comparatively little studied. However, the method has limited applicability, mainly for the cross-linking of thin-walled articles, for example, in the manufacture of tubes, oriented films, packing materials with an increased resistance to moisture and corrosive media and with a reduced gas permeability, and for the insulation of wires and cables. The mechanism of structuring by organosilanes and the composition–structure–properties relation have been little investigated.

Overall, the compositions undergoing cross linking should be the subject of vigorous studies on the basis of modern theoretical approaches and using modern methods for the investigation of the kinetics, structures, and properties of polymers, which will ensure the successful development of this field and the preparation of materials with valuable properties.

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Electrophoretic-electrochemical Deposition of Polymers and Metals

Yu.F.Deinega and Z.R.Ul'berg

The physicochemical principles of the formation of composite polymeric and metallopolymer coatings by the electrodeposition of polymer dispersions in water and electrolyte solutions are described. The electrophoretic and electrophoretic-electrochemical mechanisms for the formation of the polymer and metallopolymer coatings are examined. The role of the chemisorption interaction of the polymers and colloidal metals in increasing the protective properties of the coatings is demonstrated. The new phenomenon of "electrophoretic" polarisation and its influence on the electrode processes are considered.
The bibliography includes 100 references.

CONTENTS

I. Introduction 82
II. Electrophoretic deposition of polymer dispersions 83
III. Electrodeposition of polymers and metals 87
IV. The structure and properties of metallopolymer coatings 91

I. INTRODUCTION

The use of electric fields to form dispersed structures has been acquiring increasing importance. Particles can be oriented in electrical fields along their geometrical or molecular axes and directional movement of the particles and the interaction of polarised particles leading to structure formation can be achieved. These effects are used in electrodeposition processes,[1-4] in the manufacture of materials with anisotropic properties,[5] in the purification of liquids by electrofiltration,[6] and for controlling the mechanical properties of dispersed systems.[7]

The use of electric fields to create composite materials and coatings has opened up wide possibilities. Together with the rapid development of traditional fields of electrotechnology such as electroplating and galvanoplastics, the formation in the electric field of composite coatings based on polymers, metals, and non-metals is being applied to an increasing extent in this type of technology.

Three main trends can be distinguished in this field. The process involving the formation of coatings from solutions of oligomeric electrolytes in a constant electric field—the electrodeposition method—was developed at the beginning of the 1960's.[1-3] It is based on the formation in the electric field of a water-insoluble deposit on the anode and its subsequent thermohardening with formation of a three-dimensional polymer network from the oligomer. The mechanism of the formation of films bound by adhesion to a support includes also the formation of local bonds between groups of polymer molecules and the surface of the support.[4,5]

Numerous studies designed to create combined electrochemical coatings, which are compositions consisting of metals, alloys, and substances dispersed in them, were carried out in the same period.[6,7] The dispersed substances are refractory borides, carbides, nitrides, silicides, graphites, carbonaceous materials, abrasive powders, and lubricants. The coatings are formed as a result of the electrolytic segregation of the metal (matrix), the parallel processes involving the adhesion of the particles of the disperse phase to the matrix and their growth into the latter.

In recent years, there has been a sharp increase of interest in electrophoresis as a method of preparation of coatings formed from dispersions of various substances—polymers, metals, oxides, and natural materials.[8-12] The possibility of the simultaneous deposition and orientation of particles of different nature in order to obtain composite and especially metallopolymer coatings is of special interest.[13,14]

The introduction of colloidal metals into polymers, accompanied by the chemisorption interaction of the macromolecules with the active centres on the surfaces of the colloidal metal particles, leads to the formation of metallopolymers.[15,16] Two-phase systems stable as regards aggregation, in which the metal is uniformly distributed within the polymer, arise under these conditions. The character of the interaction of the macromolecules with the surfaces of the highly dispersed particles is determined by the chemical nature of the polymer and the metal. The macromolecules can be distributed on the surfaces of metals in the form of fixed adsorption layers, forming covalent, ionic, and coordinate bonds with the surface metal atoms.[17,18]

The formation of metallopolymer coatings in the electric field is based on the simultaneous occurrence of two processes—the electrophoretic deposition of polymer dispersions (solutions) and the electrolytic segregation of colloidal metals or alloys.[19-21] The successful development of this important branch of the electrotechnology of coatings has been promoted by fundamental studies in colloid chemistry during recent years. The creation of a theory of the polarisation of the electrical double layer and of its kinetic model, the development of a theory of the stability and coagulation of colloidal systems in an electric field, and the prediction and discovery of a number of new non-equilibrium electrokinetic phenomena—dipolophoresis, diffusiophoresis, and non-linear electrophoresis[22-26]—should be included among them.

The above theoretical developments constitute the basis of the study of the electrophoretic transport of colloidal particles, their polarisation interaction in an electric field (electrocoagulation), and electrochemical coagulation in the diffusion layer, which determine the mechanism of the formation of polymer coatings. Colloidal-chemical factors determine the possibility of regulating the conditions in the electrochemical reduction of ions and the electrocrystallisation of colloidal metal deposits.

This review considers the main principles and the mechanism of the formation of metallopolymer coatings and materials. The development of this branch of electrotechnology involves the solution of a number of problems in colloid chemistry, electrochemistry, and the physical chemistry of filled polymers. They include (1) the study of the mechanism of the formation of the charge on polymer particles and the possibility of regulating it (in connection with the electrophoretic transport and aggregation of particles on the electrode), (2) the study of the electrophoretic deposition of dispersions, especially the drift of the particles to the electrode, and of

the mechanism of the coagulation of polymer dispersions under the influence of the electric field and products of electrochemical reactions in the diffusion layer, (3) the study of the influence of the electrophoretic deposition of colloids on the polarisation of the electrode and the electrocrystallisation of the metal, (4) the study of the electrode reactions determining the deposition of metals and polymers on electrodes with a metallopolymer coating, and (5) the study of the interaction of polymers and metals in joint electrodeposition and heat treatment.

II. ELECTROPHORETIC DEPOSITION OF POLYMER DISPERSIONS

The electrophoretic deposition of dispersions includes the following stages: the charging of the polymer particles; their movement to the electrode accompanied by their aggregation in space; the coagulation of the particles in the region near the electrode; the heterocoagulation and adhesion of the particles to the electrode.

The electrodeposition of polymers from solutions involves, firstly, the movement to the electrode of macroions (polyelectrolytes) or ionised aggregates and, secondly, loss of solubility by them in the region near the cathode on interaction with precipitant ions.[3,9] Presumably, the polymer segregation process subsequently proceeds analogously to the way that this occurs in electrophoresis, including coagulation, heterocoagulation on the electrode, and the formation of a deposit which is a colloidal structure consisting of globular particles. It is important to note that both processes involving deposition from aqueous media are controlled by electrode reactions in which water is decomposed and the electrodes ionised, as a result of which an electrolyte concentration gradient is created, which is responsible for the segregation of the polymer in an insoluble form and its subsequent coagulation.

Three main mechanisms of coagulation in the electrodeposition of dispersions and the electro-osmotic compaction of the deposits formed are known at the present time: (1) electrochemical; (2) electrocoagulation; and (3) accumulative. The role of each depends on the specific physicochemical properties of the dispersed systems in the layer near the electrode and the parameters of the external electric field.

1. The Electrocoagulation Mechanism

The formation of a deposit on the electrode in an electric field is associated with the stability of dispersed systems characterised by the potential energy curves for the interaction between the particles or, in other words, by the balance of the forces acting between them. A quantitative description of the interaction of dispersed particles based on the general concept of the wedging pressure has been proposed.[24,25] Under certain conditions, two minima can appear on the overall potential energy curve for the interaction (for large and small distances between the particles) and a maximum can appear for intermediate distances. This character of the curve can be explained by the fact that the molecular and ionic-electrostatic interaction forces depend in different ways on the distance between the macroparticles: the former decrease in accordance with a power law and the latter decrease exponentially. The depth of the nearest potential well $U_{\min} \gg kT$ is determined by the degree of compensation of the molecular attractive forces by the Born repulsive forces.[26]

Coagulation, corresponding to a deep first minimum, leads to the formation of aggregates at the surface of the particle, which do not decompose after the external electric field has been switched off (irreversible coagulation). When a sufficiently high potential barrier exists, the electric field is responsible for the fixation of the particles, which corresponds to the second minimum on the potential curve. Depending on the depth of this minimum, the aggregation of the particles is reversible or irreversible.[4,27-29]

It has been shown[30] that the formation of the electrophoretic coating in the electric field is determined by the action of ionic-electrostatic forces, the repulsive forces of the non-overlapping non-deformed double layers, the dispersion attractive forces, and the dipole–dipole forces, which are manifested over distances $S = 2 + h/a$, where a is the radius of the spherical particle and h the distance between the particles. If the distances are less than a, the forces are converted into the more powerful multipolar forces due to repeated mutual polarisation, manifested solely over short distances. Allowance for the polarisation forces leads to the appearance (or deepening) of a second minimum, the depth and the coordinate of which are determined, other conditions being equal, by the strength of the active electric field.

For not unduly strong fields, where the deformation of the weakly overlapping double layers can be neglected, the total energy of the interaction between the particles is

$$U_e = U_i + U_m + U_E . \qquad (1)$$

A formula for the calculation of ionic-electrostatic repulsion U_i of the particles corresponding to arbitrary values of ϕ_δ for $\varkappa a \gg 1$ and $\varkappa a \cong \varkappa h \gg 1$ has been proposed[31] (a is the particle radius, $\varkappa$ the Debye shielding radius, and ϕ_δ the Stern potential). The molecular attraction energy U_m, expressed as a function of the distance between the particles, can be determined from the Hamaker formula for spherical particles.[32] The dipole–dipole attraction U_E can be calculated from the formula proposed by Estrela-Lopez et al.[30] The uniformity of the coating is determined by the uniformity of the packing of the particles in the film. More favourable conditions for this are created in reversible coagulation corresponding to the second minimum on the energy curve, whereupon the particles retain their ability to migrate in the film as a result of the interaction with the field and with the nearest neighbours and to fill uniformly all the cavities.[33,34] It has been shown[30] that the role of the dipolar forces increases with increasing size of the particles of the disperse phase. As the electric field strength increases, the depth of the second minimum also becomes more marked and the distance between the particle diminishes. Thus the increase in the electric field strength leads to the growth of the cohesive forces and to the compaction of the structure of the deposits.

Calculation of the potential curve for the interaction of the particles of a dielectric, semiconductors, and metals in the absence of a field and in an electric field showed that the increment in the energy of the attraction of the polarised particles under the influence of the field promotes the complete disappearance of the potential barrier.[11] At the same time, for a sufficiently high barrier, the imposition of the electric field induces the appearance of deep secondary minima responsible for further aggregation of the particles and the formation of the deposit. With increase in the electric field strength, the depth of the second minimum likewise rises.[35] In the study of the processes involving the formation of an electrophoretic coating in the region of the second minimum, it is necessary to take into account the

collective interaction of the particles in a limited or constrained volume.[4,36] Such conditions are satisfied by the layer near the electrode with an increased concentration of the disperse phase, where the particles are separated by distances comparable to their radius, which increases the attractive forces between them.[37]

In order to carry out the electrophoretic deposition, it is necessary that the electric field strength and the duration of its action should be must less than certain critical values.[38] The time necessary for the occurrence of coagulation processes is called the "critical time" τ^*. The ideas concerning the critical time have been developed in a number of studies.[11,39,40] According to Us'yarov and co-workers,[27,28] in the general case τ^* is the average statistical time required for the formation of fairly large aggregates. However, the main stage determining τ^* is the formation of a strong bond between two particles. On the basis of the slow coagulation theory allowing for the change in the concentration of particles in the space near the electrode and under conditions where a doublet is formed in the remote well, τ^* can be determined:[41]

$$\tau^* = \frac{\sum^{i} \exp\left[U(\varphi)_{max}/RT\right] \Delta\varphi_i}{64\pi^2 D r^3 N_x} , \qquad (2)$$

where r is the radius of the particle, $U(\phi)_{max}$ the potential barrier of the interaction, $\Delta\phi_i$ the specified range of values of the angle between the direction of the field and the axis of the induced dipole, D the diffusion coefficient of the particles, and N_x the concentration of the particles in the layer near the electrode.

Together with the critical time, an important characteristic of the electrodeposition process is the "critical electric field strength" E^*, i.e. the field strength for which the formation of the coagulation structure begins. It has been shown[41] that $\tau^* \propto E^{-2}$, i.e. E^* and τ^* are inter-related quantities which are functionally linked to the parameters of the system and the electrodeposition conditions. The determination of these quantities requires allowance for the polarisation interaction; otherwise there is a possibility of large discrepancies between the calculated and experimental values.[42] Examination of the aggregation of particles from the standpoint of slow coagulation[43] suggests that each pair of particles which have collided forms a doublet. The critical electric field can be estimated from the formula

$$E^* = \frac{4\pi\sigma_0}{\varepsilon_0} , \qquad (3)$$

where σ_0 is the electrical conductivity of the medium and ε_0 the dielectric constant. The aggregation of particles in the layer near the electrode is accelerated not only by an increase in the electric field strength but also following an increase in the concentration of the suspension.[41]

The question of the interaction of the particle with the surface of the electrode is no less important. It follows from the heterocoagulation theory that the optimum deposition conditions are ensured for unlike charges of the electrode and the particle.[44] When the signs of the charges are identical, the wedging pressure plays an appreciable role.[41] The interaction of the particle with the electrode is regarded[45–47] as the result of the attraction due to the image forces, which are dipolar in nature. A formula has been obtained according to which the dipolophoretic attraction becomes significantly greater than the electrophoretic force with decrease in the distance to the electrode surface. The attractive forces are proportional to the radius of the particle raised to the sixth power.

The role of the electrocoagulation mechanism in the formation of coatings in aqueous organic media was tested experimentally by investigating the dependence of the yield of the deposit on the polarisation of the particles of the disperse phase.[48] In the isopolarisation state, the polarisation criterion is described by the expression

$$\mathrm{Rel}_{iso} = \frac{\cosh\frac{\varphi_\delta}{2} - 1}{\varkappa a} = \frac{1}{2} . \qquad (4)$$

The electrophoretic deposition of an aerosol dispersion in isopropyl alcohol—water mixtures with an increasing water content has been investigated.[48] In the absence of dipolar interaction between the particles and the electrode, in the isopolarisation state the yield of the deposit formed via the electrocoagulation mechanism is minimal. Studies have shown that a change in the composition of the dispersion medium can serve as a fine instrument for varying the contribution of the electrocoagulation and the electrochemical mechanisms to the electrophoretic deposition of dispersions. Thus it is possible to regulate the process involving the formation of the coatings and the structure and properties of the latter.

2. The Electrochemical Mechanism

The electrochemical mechanism presupposes the formation, in the zone near the electrode, of an excess electrolyte concentration front which spreads into the surrounding space; these ideas date back to two studies.[38,49] In the above mechanism the critical time τ^* is interpreted as the time necessary to create the threshold electrolyte concentration at which the stability of the system decreases and the particles coagulate on the electrode in conformity with the Deryagin–Landau–Verwey–Overbeek (DLVO) theory.[24,25,50,51] The excess electrolyte concentration in the diffusion layer at the electrode c_{el} tends to the initial concentration c_0 under conditions such that the concentration of ions changes as a result of diffusion and electromigration:[49]

$$c_{el} \to c_0 = \frac{2}{\pi^{1/2}} \frac{It_m}{SF} \left(\frac{\tau}{D}\right)^{1/2} , \qquad (5)$$

where I is the current, t_m the transport number of the ions M^+, D the diffusion coefficient of the ion pair M^+OH^-, S the electrode surface area, F the Faraday, and τ the deposition time.

The formula for τ^* can be represented in the form

$$\tau^* = pI^{-2} = qU^{-2}\sigma^{-2} \qquad (6)$$

where p and q are constants, U is the potential, and σ the conductivity of the suspension. Thus the critical time is inversely proportional to the square of the potential of the electrodes and to the conductivity of the suspensions. The experimental confirmation of these relations is one of the proofs of the validity of the theory considered. The DLVO theory, developed for systems with a conducting dispersion medium, can also be used to calculate parameters which determine the stability of dispersions in the region near the electrode in a weakly conducting non-polar dispersion medium.[38,49]

The ideas concerning the role of the electrochemical mechanism of the coagulation of particles in the formation of a deposit were developed further in other investigations.[2,52,53] Analysis of the experimental and theoretical data shows that the electrophoretic deposit is formed in two stages and that the process includes the transition from reversible to irreversible coagulation and also an increase in the concentration of the

polymer and electrolyte species in the diffusion layer near the electrode. Electrochemical coagulation can therefore take place via a concentration mechanism (determined by the compression of the electrical double layer) and a neutralisation mechanism (associated with a decrease in the charge).

The degree of reversibility of the coagulation and hence the thickness and strength of the deposit are determined by the spatial-temporal distribution of the coagulating ions in the zone near the electrodes. The relations illustrated in Fig.1 give an idea of the processes involving the formation of deposits from the polymer particles.[53] The factor determining the kinetics of the formation of the deposit is the change in the overall concentration of the coagulating ions, in the given instance hydroxide ions. With increase in the electrolyte content in the diffusion layer (Fig.1*a*, curve *1'*), the dimensionless electrokinetic potential $\tilde{\zeta} = (F/RT)\zeta$ decreases (curve *1*) owing to the compression of the double layer.

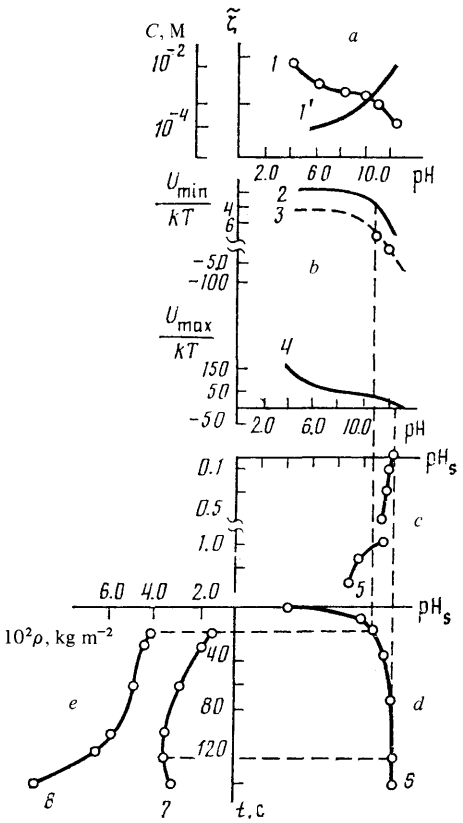


Figure 1. *a*) Dependence of the electrokinetic potential (ζ) of the particles of an epoxide oligomer (curve *1*) and of the electrolyte concentration (curve *1'*) on the pH; *b*) dependence of the energy of the interaction of a particle doublet under the usual conditions (curve *2*) and under constrained volume conditions (curve *3*) and of the potential barrier preventing aggregation (curve *4*) on the pH; *c*) variation of the pH of the dispersion in the layer near the electrode with the distance *l* to the electrode 40 s after the onset of deposition; *d*) variation of the pH in the layer near the electrode with deposition time; *e*) dependence of the yield of the deposit (ρ) formed as a result of irreversible aggregation only (curve *7*) and as a result of the joint reversible and irreversible aggregation (curve *8*) on deposition time.[53]

The decrease in the potential ζ in coagulation of the concentration type deepens the remote potential well (Fig.1*b*, curves *2* and *3*) and decreases the potential barrier (curve *4*). The probability of the long-range (reversible) and short-range (irreversible) coagulation of the particles increases correspondingly. The first stage in the deposition process is intense reversible coagulation. After 20 s, the pH increases from 3.8 to 11.0 near the electrode (Fig.1) to 8.0 at a distance of 0.3 mm from the electrode. The subsequent increase in pH is determined by the balance between the formation of OH^- ions in electrolysis and their consumption in diffusion and migration processes. At a distance $l = 0.5$ mm from the electrode, the pH has constant values, while in the presence of polymers the pH decreases appreciably (Fig.1*c*).

At pH 11.0 the ζ potential is 0.9 (Fig.1*a*, curve *1*) and the potential barrier U_{max} is still fairly high (Fig.1*b*, curve *4*). However, the binding energy of the particles U_{min}, determined by the depth of the remote potential well recalculated to give the number of nearest particles, is entirely sufficient for their mutual fixation (Fig.1*b*, curve *3*). The fraction of the reversible deposit exceeds appreciably that of the irreversible deposit (Fig.1*e*). The deposit is readily peptised after the removal of the field.

With increase in the electrodeposition time and with increase in pH at the electrode surface from 11.0 to 12.2, the ζ potential falls to 0.45 (Fig.1*a*, curve *1*). This threshold value of the ζ potential corresponds to the onset of irreversible coagulation. The potential barrier preventing the coagulation of particles then disappears (Fig.1*b*, curve *4*). The yield of the irreversibly coagulated deposit at high pH becomes a maximum (Figs.1*c*, 1*d*, and 1*e*). The overall yield of the deposit also increases (Fig.1*e*, curve *8*); with increase in pH, the reversible coagulation begins at a certain distance from the electrode and the deposit is partly formed from aggregates weakly bound to the electrode. The amount of the irreversibly coagulated deposit then falls.

Analysis of systems with the neutralisation type of electrochemical coagulation showed that their principal feature is a large contribution by irreversible coagulation to the deposit formation process.[54] The deposition from such dispersions proceeds almost without a critical time.

Systems with the concentration type of electrochemical coagulation are more plastic in the sense that there is a possibility of controlling the kinetics of the deposit formation on the electrode, but the process is in this case longer and the amount of deposit formed is smaller than in systems of the neutralisation type. The concentration systems are most suitable for the preparation of high quality electrophoretic deposits. The electrochemical purification of the liquid is best performed by the electrochemical coagulation of the neutralisation type.

3. The Accumulative Mechanism

The electrophoretic deposit is formed via the accumulative mechanism as a result of the coagulation of particles at the electrode under the influence of the forces developed by the external electric field and the molecular attraction forces. It has been suggested[55] that the process involving the preparation of a deposit by the electrophoretic method is analogous to the sedimentation of particles in the gravitational field. The role of the electric field is to supply particles to the electrode and to compact the deposit on the electrode surface. According to the accumulative theory,[55] a distinctive feature of this mechanism is the direct proportionality of the critical deposition time τ^* to the square of the field strength and its inverse proportionality to the concentration

of particles. This mechanism makes a significant contribution to the formation of a deposit from concentrated systems and in the case of dilute dispersions it is manifested in the zone near the electrode to a greater extent the higher the content of the disperse phase under the constrained volume conditions. The principle postulates and conclusions concerning the accumulative mechanism have been described in detail.[1,55,56]

All three deposit formation mechanisms are accompanied by the electro-osmotic compaction of the deposit,[11] which is an additional factor in the formation of the coating. The electro-osmotic component must be manifested appreciably as the deposit becomes denser and its thickness increases. It alters the distribution of the concentration of the particles in the region near the electrode, which leads to the appearance of a clarified layer of dispersion medium at the upper boundary of the deposit being formed. The liquid in the layer moves upwards and entrains the dispersed particles of the suspension, some of which contribute to the growth of the electrophoretic deposit. It has been shown[57] that the electrokinetic potential calculated from the flow rate of the medium in concentrated suspensions approaches the ζ potential determined by the electro-osmotic method. Thus the formation of the electrophoretic deposit is accompanied by the electro-osmotic migration of the dispersion medium, which promotes, on the one hand, an increase in the density of the layer of suspension near the electrode and, on the other hand, it inhibits the motion of the particles, since it is directed in opposition to it. Estimation of the electro-osmotic compaction forces showed that they increase with increasing concentration of the dispersion phase.[57]

4. Cataphoretic Deposition of Polymer Dispersions

In the conclusion of this Section, we shall consider the characteristic features of the electrophoretic deposition of polymer dispersions on the cathode (for aqueous organic suspensions of epoxide and phenol-formaldehyde oligomers).[48] The character of the electrochemical coagulation—neutralisation or concentration—plays a significant role in the deposit formation process. The results of the study of the electrophoretic deposition of the epoxide oligomer via the concentration mechanism and of the phenol-formaldehyde oligomer via the neutralisation mechanism from an aqueous organic medium are presented in Table 1. Evidently there are fundamental differences in the formation of deposits via the two mechanisms.

The deposition of the epoxide oligomer begins after a critical time, amounting to 20 s, has elapsed, which is associated with the attainment in the diffusion layer of the pH necessary for coagulation (in the given instance 11.0). It is noteworthy that coatings based on the epoxide oligomer are formed in two stages: reversible and irreversible coagulation. The duration of the first stage is between 20 and 50 s and that of the second between 60 and 120 s. The two-stage nature of the deposition process is a necessary precondition for the preparation of a uniform coating, since favourable conditions for the distribution of particles over the entire area of the electrode are created in reversible aggregation. The deposit is fixed in the irreversible coagulation stage. The phenol-formaldehyde oligomer is deposited immediately without a critical time.[48] The formation of the coating is caused mainly by irreversible coagulation. A common feature of the systems investigated is the formation of a deposit within the limits of the diffusion layer. In the course of the formation of the deposit, the ratio of its components, formed as a result of the reversible and irreversible coagulation, changes with time and there is an overall tendency towards an increase in the yield of the polymer. The ratio of the reversible and irreversible aggregations makes it possible to determine the parameters of the deposition process (cathodic current density, deposition time, and field strength) for which the optimum properties of the coating are attained.

Table 1. Parameters of the processes involving the electrophoretic deposition of polymers from an aqueous organic medium via the concentration and neutralisation coagulation mechanisms.

t, s	pH_s	$10^2\rho_1$, kg m^{-2}	$10^2\rho_2$, kg m^{-2}	l, mm	δ, mm
Epoxide oligomer*					
2	6.50	0.45	0.60	0.70	0.01
5	8.60	0.80	0.96	0.80	0.016
10	9.80	1.1	1.30	0.85	0.018
20	11.00	1.50	2.00	0.90	0.025
80	11.80	3.20	1.30	1.10	0.025
140	12.20	3.00	5.80	1.10	0.055
Phenol-formaldehyde oligomer**					
2	6.15	0.41	0.11	0.40	0.010
10	8.80	0.88	0.24	0.50	0.016
30	10.70	6.20	2.60	0.85	0.055
40	10.80	6.00	3.20	0.85	0.070

Notation: t is the deposition time, pH the pH value near the electrode, ρ_1 the yield of the irreversible part of the deposit, ρ_2 the yield of the reversible part of the deposit, l the thickness of the diffusion layer, and δ the thickness of the coating.

* Concentration coagulation.
** Neutralisation coagulation.

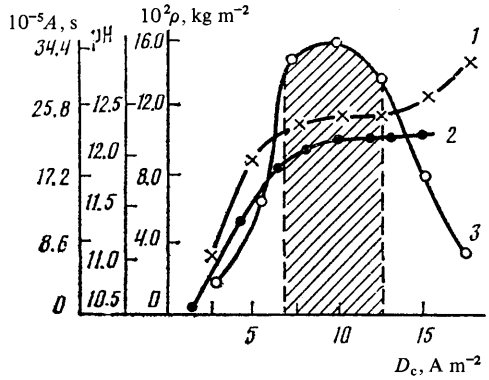


Figure 2. Dependence of the yield (ρ) of the electrophoretic deposit of an epoxide oligomer (curve *1*), of the pH of the layer near the electrode (curve *2*), and of the corrosion stability (A) of the coatings (curve *3*) on the cathodic current density.[48]

Fig. 2 presents the dependence of the yield of the deposit of the epoxide oligomer, the pH of the diffusion layer, and the corrosion stability of the coatings on the cathodic current

density. Since the electrode deposition process is an electrode reaction, I = const. is a necessary condition. The cathodic current density D_c is chosen so that it is possible to regulate the conditions in the electrochemical reactions determining the course of the coagulation processes. The increase in D_c in the initial section is accompanied by a parallel increase in the pH of the diffusion layer, the yield of the deposit, and the corrosion stability of the coatings in a chamber with 100% humidity. The increase in the amount of deposit and the pH ceases after the attainment of pH 12.2. The region $D_c = 7-12$ A m^{-2}, corresponding to the maximum stability of the films in the corrosion medium (shaded in Fig. 2), also corresponds to the transition from reversible to irreversible coagulation (pH 12.2). The decrease in the anticorrosion stability at $D_c > 12$ A m^{-2} is associated with the intensification of the electrochemical reactions, the spreading to the bulk phase of the increased electrolyte concentration front, and the deposition on the electrode of the large aggregates of particles formed under these conditions. This entails the growth of the yield of the deposit and the simultaneous increase in its porosity. Thus there is a direct relation between the deposit formation conditions, the relative contributions of the reversible and irreversible coagulation, and the corrosion stability of the coatings (Fig. 2 and Table 1). The methods for the preparation of composite polymer coatings with anticorrosion, protective-decorative, and electrically insulating properties have been described.[58-62]

III. ELECTRODEPOSITION OF POLYMERS AND METALS

1. The Mechanism of the Formation of Metallopolymer Deposits

The metallopolymer deposits are formed as a result of the simultaneous electrodeposition of polymer dispersions and the electrochemical segregation of the metal. The electrophoretic precipitation of the polymer deposit and the interaction of the particles of the disperse phase in the zone near the electrode play a decisive role in this process. The electrodeposition and electrocrystallisation of the metal depend in their turn on the kinetics of the formation of the polymer layer on the electrode. The structure of the metallopolymer deposit is determined by the character of the polarisation and chemisorption interactions between the polymer and metallic particles.

In this connection, we shall consider the mechanism of the formation of metallopolymer coatings from the standpoint of the influence of surfactants and polymers on the discharge of metal ions and the formation of colloid deposits. The process involving the formation of the metallopolymer deposit on the electrode begins with the formation of a polymer layer through which metal ions move to the electrode as if through a membrane. The supply of ions to the electrode surface is the rate-limiting stage. The influence of the polymer layer on the metal ion reduction process is determined by the concentration of the disperse phase, the charge on the polymer particles, their size, and the deposition conditions. The conditions governing the creation of a controllable flux of metal ions migrating to the cathode and the interaction between the particles of the segregated polymers and metals determine the composition and structure of the deposits.

The homocoagulation and heterocoagulation interactions between the polymer and metallic particles depend on the colloidal-chemical properties of the system and on the deposition conditions.[1] If the polymer particle is deposited on a metallic particle (heterocoagulation) in the formation process, then the growth of the metallic particle is greatly inhibited. In the case where the polymer particles interact mainly with one another during deposition (homocoagulation), metallic particles are formed and grow freely. The relative contributions of homocoagulation and heterocoagulation are determined by the balance between the electrophoretic (F_{ef}) and dipolophoretic (F_d) forces. When a deposit is formed from dispersions characterised by high electrokinetic potentials of the particles, low electrolyte concentrations, and the quantity Rel > 1, it is found that $F_d/F_{ef} > 1$. The active inhibition of the electrocrystallisation of the metal under these conditions makes it possible to segregrate the metal in the form of particles of highly dispersed powders uniformly distributed within the polymer. In the codeposition of particles of the epoxide oligomer and lead, the latter are produced with an irregular form and their size is 0.1–0.3 μm.[1]

In the electrodeposition of dispersions with a low ζ potential and with the parameter Rel ≪ 1, we have the ratio $F_d/F_{ef} < 1$. The structure of the deposit changes significantly in this case, since the polymer being deposited inhibits to a lesser extent the growth of metallic particles. They are needle-shaped and their size is up to 2–5 μm. Under these conditions, there is a possibility of obtaining coatings with a high metal content (up to 90–96%) and a thickness up to 100 μm, since the metal dendrites formed are conducting.

The ideas described above concerning homocoagulation and heterocoagulation can explain the results obtained in the experimental study of the codeposition of polymers and metals. A general tendency is an increase in the yield of the deposit with increasing concentration of the disperse phase and charge on the particles and a decrease in the metal content of the latter. An increase in the electrolyte concentration naturally diminishes the potential and also increases the parameter a and decreases Rel. Dipolophoresis and electrophoresis promote the homocoagulation of the polymer particles. The growth of metallic particles is not blocked, which increases the metal content in the deposit.

With increase in the concentration of polymer particles and their charge, the simultaneous occurrence of dipolophoresis and electrophoresis promotes the interaction of the polymer and metallic particles, i.e. heterocoagulation. The effect, involving the blocking of the electrode surface and of the metallic particles by the polymer particles, leads to the appearance of a new form of overpotential, which we have called the electrophoretic overpotential. The electrophoretic overpotential influences the electrocrystallisation of the metal as a rule to a much greater extent than the adsorption of a surfactant on the electrode.[18,63,64-67]

Fig. 3 illustrates the polarisation curves for a copper electrode in 0.032 M $Cu(HCOO)_2$ solution containing a biquaternary ammonium compound and a dispersion of the organosilicon oligomer. The joint action of the surfactant and the polymer results in the discharge of the copper ions under the conditions of appreciable cathodic polarisation. At low current densities, a shift of the polarisation curves towards negative potentials is already observed: by 220 mV in the presence of the surfactant and by 480 mV in the presence of the polymers. When the quaternary ammonium compound (Fig. 3, curve *2*) and the disperse phase (curves *3–5*) are introduced, the current maxima on the curves are reduced and sections appear along which the current depends little on the potential. This indicates an increase in the activation energy necessary for the penetration of metal ions through the polymer layer and their discharge on the electrode.

The electrophoretic polarisation depends directly on the colloidal chemical properties of the dispersions deposited, which determine the relative contributions of homocoagulation and heterocoagulation in the deposit. Table 2 presents the most typical data characterising the codeposition of dispersions and colloidal metals. The electrophoretic polarisation increases with increasing ζ potential of the polymer particles. The increase in the electrokinetic potential increases in its turn Rel and heterocoagulation.[18] For example, the increase in the ζ potential of the epoxide oligomer particles from +36.2 mV to +115.5 mV corresponds to a change in Rel from 0.12 to 0.87.

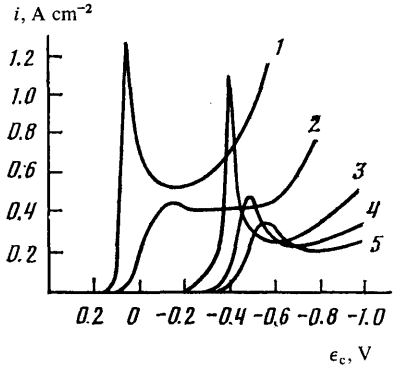


Figure 3. Cathodic polarisation curves for a copper electrode: *1*) in 0.032 M $Cu(HCOO)_2$ solution; *2*) ditto with added 0.5 mm surfactant; *3*) ditto with added disperse phase [*3*) 0.125%; *4*) 0.25%; *5*) 0.50%][83] (*i* is the current density and ϵ_c the potential).

Table 2. The influence of the ζ potential of the epoxide oligomer particles and their concentration on the polarisation of the electrode in codeposition with lead [electrolyte 0.005 M $Pb(HCOO)_2$].[19,68]

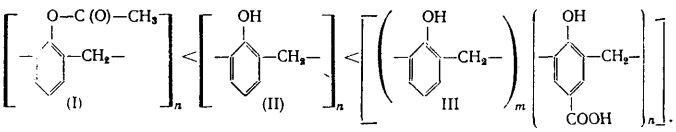
ζ potential, mV	Shift of polarisation curves, V	Concentration of disperse phase, wt.%	Shift of polarisation curves, V	Yield of polymer component, mg cm^{-2}
−36.2	0.8	0	0.1	0
+43.7	0.9	0.06	0.35	6.4
+54.0	1.1	0.31	1.4	8.3
+84.8	1.3	0.94	1.9	10.1
+115.5	1.6	2.25	2.6	12.8
		2.6	3.3	12.1

The next factor determining the effectiveness of the increase in the overpotential of the segregation of metals in the formation of the metallopolymer deposit is the increase in the concentration of the disperse phase in the electrolyte solution.[68] Thus the increase in the epoxide oligomer concentration increases the polymer content in the metallopolymer deposit and leads to the growth of the lead reduction overpotential, which is indicated by the shift of the polarisation curves towards negative potentials by 3 V (Table 2); under these conditions the metal is produced in a highly dispersed state.

The effective activation energy for the discharge of lead ions increases from 28 to 74 kJ mol^{-1} with increase in the concentration of the disperse phase from 2.5 to 5 wt.%.[18] This is accompanied by a decrease in the size of the metal particles from 2–3 μm to 0.2–0.5 μm and a change in the crystal structure; the size of the blocks of the mosaic falls from 1590 to 200 Å.

Not only the polarisatio. interaction between the polymer and metallic particles but also the chemisorption interaction processes between them play an important role in the establishment of the conditions governing the polarisation of the electrode. In the process involving joint segregation on the electrode, the epoxide oligomers interact with the surface of the lead particles with opening of the epoxide rings.[15] For example, a 2.2 V cathodic shift of the polarisation curves has been observed for epoxide oligomers containing 2.2% of epoxide groups, while in the presence of an epoxide content of 21.8% the shift was by 3.4 V other conditions being equal. The displacement of the epoxide groups in the oligomer chain by hydroxy-groups reduces this effect to 0.7–0.9 V.

Analogous results have been obtained in the electrodeposition of dispersions of phenol-formaldehyde oligomers and zinc.[65,66] When oligomers with hydroxy- and carboxy-groups and oligomers in the chains of which these groups have been replaced by ester moieties are used, the zinc electrocrystallisation overpotential increases in the sequence



The chemisorption interaction between the polymer and metallopolymer particles has two important consequences: firstly, together with the increase in the ζ potential of the polymer particles and in their concentration, this is a fine instrument for regulating the degree of dispersion and the structure of cathodic metal deposits and, secondly, as will be shown below, the formation of surface compounds and the shielding of such surfaces of metallic particles constitute the basis of corrosion stability of metallopolymer coatings.[1,56]

An increase in polarisation and hence a decrease in the metallic particle size have been noted in the codeposition of zinc with phenolformaldehyde oligomers of type (III) with increase in their content of carboxy-groups from 2 to 16%.[67] The increase in polarisation indicates a significant change in the rates of both principal stages of the metal segregation process: the penetration of metal ions to the electrode and their discharge.

The change in the polarisation of the electrode is caused by the joint influence of the biquaternary ammonium salts and polymer particles on the parameters of the electrical double layer and the diffusion layer at the electrode. The adsorption of surfactants plays an important role in the initial period of the formation of the metallopolymer deposit, influencing the electrical double layer at the electrode surface.[64] As a rule, the formation of the adsorption layer is accompanied by a decrease in the exchange current and an increase in the surface coverage, which reaches the limiting value of 0.87 at a surfactant concentration of 2 M.[64]

Thus examination of the data obtained permits the conclusion that the characteristic feature of the segregation of the metal in the formation of the metallopolymer deposit consists in the fact that it occurs under the conditions of very pronounced adsorption and electrophoretic concentration polarisation. The rate-limiting stage of the process becomes the diffusion of metal ions M^{2+} through the polymer layer.

The diffusion boundary layer is localised within the deposit. A steady state reaction is established after the attainment of a constant thickness of the latter. Up to this instant, the process is non-stationary, the thickness of the diffusion layer increases with time, and the balance between the rate of the electrochemical discharge of metal ions and the rate of their supply and also between the concentrations of the discharging ions and ions diffusing into the solution is disturbed. The electrochemical reaction proceeds in accordance with the general laws of the diffusion kinetics of heterogeneous processes in solutions.[71,72] The thickness of the diffusion layer reaches ~500 μm under the conditions of the electrophoretic deposition of polymers and the electrochemical segregation of the metal, which agrees with data obtained in an unstirred solution[73] and is close to the values which have been obtained in the study of processes involving the electrophoretic deposition of polymers (Fig.1). The principal characteristic feature of the formation of such a layer in a combined process consists, in contrast to the processes involving the segregation of pure metals, in slow diffusion into the bulk phase and an appreciable accumulation of OH^- ions in the layer near the electrode.

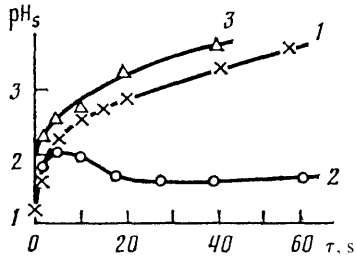


Figure 4. Dependence of pH_S on the electrodeposition time (τ) for a dispersion of a phenol-formaldehyde oligomer (curve *1*), lead (curve *2*), and the metallopolymer deposit based on them (curve *3*).[74]

The principal differences between the formation of the diffusion layer on deposition of metals, polymers, and metallopolymers are illustrated in Fig.4, characterising the variation of the pH in the layer near the electrode (pH_S) as a function of the process time in the codeposition of dispersions of phenol-formaldehyde oligomers and lead from solutions of lead sulphamate.[74] Studies of the variation of the pH of the layer near the electrode (pH_S) showed that the formation of a polymer film, which prevents the diffusion of OH^- ions into the bulk of the solution, leads to an increase in the pH of the diffusion layer compared with the segregation of the pure metal (without the polymer), which retards the onset of the stationary state. Analogous results have been obtained in the deposition of other resins, including the aminoformaldehyde resin.[56] An increase in pH_S leads to the segregation of metallic deposits with different phase compositions and the formation of hydrates and basic salts.[1,18,74]

The character of the diffusion processes and hence the mechanism of the formation of metallopolymer deposits are determined mainly by the relative contributions of the electrophoretic and electrochemical depositions. A transition from metallopolymer deposits to composite electrochemical coatings with a high metal content can be achieved by regulating them by varying the concentration of the disperse phase, the charge on the particles, and the concentration of the electrolyte. In the first case, the polymer is deposited preferentially: the rate of its electrophoretic deposition exceeds the rate of the electrochemical segregation of the metal.[75] Then the parameter A, characterising the ratio of the segregated polymer and metal, assumes the value $A \leqslant 0.25$. This corresponds to the conditions for electrodeposition from dilute electrolytes and to increased electrokinetic potentials of the particles in the dispersions and their concentrations (mechanism I). By varying these parameters, it is possible to equalise the rates of electrodeposition of polymers and metals and to obtain deposits of a constant composition, with respect to thickness, and a uniform structure. If the rate of segregation of the metal exceeds the rate of deposition of the polymer, composite coatings are formed, consisting of a metallic matrix in which the polymer particles are distributed (mechanism II). The presence of a kinetic potential of the polymer particles in concentrated electrolyte solutions indicates the important role of electrophoretic transport of the particles of the disperse phase in the formation of metallopolymer electrochemical coatings via mechanism II.[76,77]

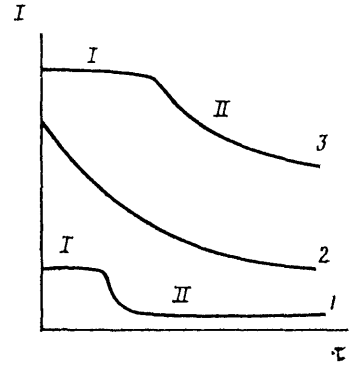


Figure 5. Schematic illustration of the dependence of the current on the time required for the deposition of polymers (curve *1*) and metallopolymer deposits from dilute (curve *2*) and concentrated (curve *3*) electrolytes.

The differences between these two processes, the first of which is determined by diffusional kinetics and the second by electrochemical kinetics, are revealed when the dependences of the current I on the deposit formation process time are compared (Fig.5). The joint deposition of the polymer and the metal via mechanism I (curve *2*) is characterised by the absence of a critical time, which is the case in the electrophoretic deposition of the polymer (curve *1*) and by an appreciable decrease in the current. The decrease in τ^* is promoted by an increase in the electrolyte concentration (OH^-) even in the first seconds as a result of electrode reactions and the rapid segregation of the metallic deposit. The sharp decrease in the current can be explained by its proportionality to $\tau^{1/2}$, which is associated with the shielding effect of the polymer deposit and with the decrease in the diffusion of M^+ ions through the polymer layer formed.

The presence of a horizontal section on the curve in the codeposition of metals and polymers from concentrated electrolytes (Fig.5, curve *3*) is associated with the preferential

segregation of the metal. The extent of the first horizontal section is limited by the time during which the composition and conductivity of the deposit remain constant. The conditions under which the resistance of the film is independent of time in the initial deposition stage, which ultimately determines that the current is independent of time, have been estimated.[75] In the deposition process, these conditions break down and, after a certain time interval, the deposit is formed under conditions where $I \propto \tau^{1/2}$, in conformity with mechanism *I*. These ideas have been confirmed by data obtained from layer-by-layer analysis.[74] The greatest metal content in the metallopolymer deposits obtained in the deposition of the phenol-formaldehyde oligomer from concentrated zinc sulphate solutions has been detected in the lower layers, the upper layers being enriched in the oligomer (Table 3).

Table 3. Results of the layer-by-layer chemical analysis of metallopolymer coatings.[74]

Coating deposition time, s	5	10	17	25	30
Thickness of coating, μm	4	6—7	10—12	14—16	20—22
Zinc content, wt.%	92	87	82	78	69

The occurrence of the conditions for diffusional kinetics in the formation of metallopolymer coatings via mechanism I follows from the estimation of the diffusion of metal ions in the deposit formation process from the equation for nonstationary diffusion for planar electrodes.[75] Here it was assumed that (1) the thickness and mass of the deposit are limited by the conditions for adequate ionic conductivity in the pores within the deposit, i.e. by the presence of metal ions in a polar dispersion medium, (2) the main bulk of the ions are supplied to the electrode surface through the polymer layer via diffusion, (3) the rate of deposition of the polymer exceeds the rate of segregation of the metal ($A \leq 0.25$), and (4) since diffusion takes place in a porous body, i.e. is independent of the migration of the dispersion medium, convective diffusion is ruled out.

The boundary conditions are determined by the fact that, after a certain time has elapsed, the concentration of ions on the electrode surface becomes zero because their diffusion through a film of large thickness is impossible. The film is formed in the presence of M^+ ions being discharged simultaneously with the deposition of the polymer.

For thin films under the conditions of long deposition times, the relation between the film thickness and the deposition time is given by the equation[7]

$$l = \left(\frac{2Dc_0\tau}{M}\right)^{1/2}, \qquad (7)$$

where *M* is the concentration of metal ions within the moist film, c_0 their concentration at the electrode surface, and *D* the diffusion coefficient of the ions. This relation has been confirmed experimentally in a study of the codeposition of an epoxide oligomer with lead.[75] The thickness of the deposit and the Faraday current are described by $l \propto \tau^{1/2}$ and $I \propto \tau^{1/2}$ respectively.

In the electrochemical reduction of metals in polymer dispersions stabilised by surfactants, the conditions for the transport not only of ions but also of polymer particles, i.e. the ζ potential, change. The introduction of small amounts of polyvalent electrolytes (10^{-5}—10^{-4} M) into the polymer dispersions stabilised by added surfactants increases the electrokinetic potential of the polymer particles as a result of the additional adsorption of the codeposited cations M^{2+}.[78] This possibility has been justified theoretically in a study[79] where it was shown that the degree of sorption of the codeposited ions is determined by the product $z\phi_\delta$ (where *z* is the valence of the ion) and diminishes sharply for $\overline{\phi}_\delta > 3$—4 as a result of the enhancement of the electrostatic repulsion. The sharp decrease in the ζ potential of the particles and in the stability of the system as regards aggregation occur for electrolyte concentrations 10^{-3}—10^{-2} M. Furthermore, the introduction of electrolytes into polymer dispersions, stabilised by surfactants, can promote an increase in the electrokinetic potential of the particles as a result of the additional adsorption of the surfactant on their surface and the compaction of the adsorption layer.[80—82] As a rule, with increase in the electrolyte concentrations, the ζ potentials pass through a maximum. The characteristic features of ion transport under these conditions are associated with the fact that the particles of the disperse phase behave as ion carriers, which makes a definite contribution to their diffusion to the electrode. The efficiency of the ion transport is determined by the magnitude and sign of the charge on the particles (ϕ_δ) and by the degree of adsorption of the surfactant.

Table 4. Dependence of the diffusion coefficient *D*, the thickness of the diffusion layer δ, and the thickness of the coating *l* on the electrolyte composition in the formation of a metallopolymer coating based on an organosilicon oligomer and copper.[63,64]

Parameter	Copper formate	Copper formate + 0.5% of oligomer dispersion	Copper formate + 0.5% of oligomer dispersion + surfactant at different concentrations, mM			
			0.13	0.50	1.00	3.00
$10^6 D$, $cm^2 s^{-1}$	1.62	2.37	1.90	1.53	1.42	1.12
$10^2 \delta$, cm	0.326	0.457	0.366	0.295	0.274	0.216
$10^2 l$, cm	—	—	0.34	0.28	0.26	0.22
$10^3 i_d \tau^{1/2}$	14.5	16.8	15	13.5	13.0	11.5

The estimation of the diffusion coefficients from Sand's equation, which is valid for linear semi-infinite diffusion,[83] showed that the introduction of particles of an organosilicon oligomer increases the diffusion coefficient of the Cu^{2+} ions (Table 4). The results obtained suggest that this effect is associated with the transport of ions by polymer particles. With increase in the surfactant concentration and hence in the positive ζ potential of the particles, the effect involving an increase in the diffusion coefficient of the Cu^{2+} ions disappears. Apparently a phenomenon somewhat similar to that of micellar catalysis, described in the literature,[84] takes place here, but, instead of surfactant micelles, the ion carriers are polar particles stabilised by such micelles. When the system contains ionogenic surfactants and cations, the charge on the particle is generated as a result of the competitive adsorption of both types of species.

The introduction of biquaternary ammonium compounds decreases the degree of adsorption of the cations on the surface of the particles.[64] With increase in the surfactant content and hence in the ζ potential, the additional sorption of the codeposited cations becomes impossible, which decreases the diffusion coefficient by a factor of two (Table 4). The

limiting diffusion current i_d changes analogously. Evidently there is a correlation between the diffusion coefficient D and the thickness of the diffusion layer δ. Comparison of the values of δ with the thickness of the coatings l shows that the coatings are formed within the limits of the diffusion layer.

The steady increase in the diffusion of the ions M^{2+} entails a decrease in the potential at which the metal is segregated at low concentrations of the disperse phase and an acceleration of the deposit formation process.[85,86] Apart from the intensification of ion transport to the electrode by virtue of the involvement of the polymeric carriers in the process, this phenomenon can be accounted for by the enhancement of the diffusion under the conditions of the simultaneous segregation of the metal and polymer particles. The formation of a three-dimensional-network of dielectric particles can lead to the deformation of the electric field strength lines in the interelectrode space and hence to an intensification of the field in the gap between the particles.

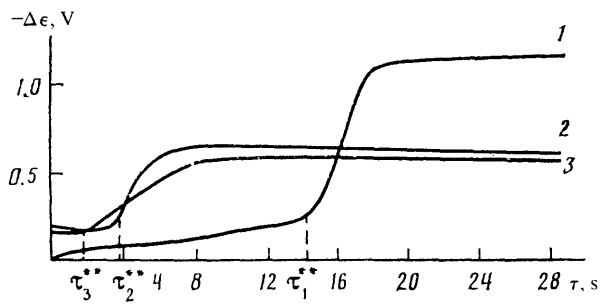


Figure 6. Time variation of the potential of a copper electrode (galvanostatic conditions) in 0.032 M $Cu(HCOO)_2$ solution containing 1% of the disperse phase and also different amounts of a surfactant [*1*) 0%; *2*) 0.75%; *3*) 2%] (D_c = 8.9 A m^{-2} is the cathodic current density).

Yet another important aspect of the mechanism of the joint deposition of polymer and metal dispersions is noteworthy. It consists in the fact that the presence of polymer particles in the diffusion layer promotes, like surfactants, a change in the electrode potential and hence in the energy parameters of the metal segregation process. In the electrophoretic-electrochemical codeposition of an organosilicon oligomer and copper in the presence of an uncharged oligomer dispersion, the electrode potential shifts appreciably towards negative values after the transient time has elapsed.[63] In the codeposition of copper with dispersions whose particles have a high ζ potential, the electrode potential diminish by a factor of 2–3 with increase in the polymer concentration (Fig. 6, curves *1* and *3*). The electrode reactions begin at higher potentials of the cathode and require an appreciable polarisation, the contributions of its individual components changing in different stages of the process. At a low current density, where the M^{2+} ions are reduced at constant (or nearly constant) potentials, the rate of the electrochemical reaction is apparently lower than the rate of diffusion of ions to the electrode surface. An appreciable overpotential, due to charge transfer, is observed. The study of the temperature dependence of the rate of the electrochemical reaction at different current densities showed that the overpotential associated with the formation of a new phase also makes a significant contribution.[64]

The nature of the overpotential and the possibility of regulating it throughout the deposit formation process determine the structure of the layer of the deposited material. At current densities close to or exceeding the limiting values, copper is deposited on the cathode in the form of a dense layer in the course of a short period equal to the transient time τ^{**}, which, as can be seen from Fig. 6, is appreciably reduced with increase in the charge on the polymer particles (τ_1^{**}, τ_2^{**}, and τ_3^{**} respectively). After the time τ^{**} has elapsed, the concentration of the discharging ions in the region near the cathode falls, the potential shifts towards more negative values, and copper is subsequently deposited in a non-compact form.

Thus, by altering the concentration of the particles of the disperse phase and their charge, it is possible to regulate the parameters of the diffusion layer and hence the reduction of the metal ions. It becomes possible to carry out the electrocrystallisation process under conditions of increased activated inhibition and high polarisation.

In connection with the formation of metallopolymer coatings via mechanism II, the phenomenon of the electrophoretic mobility of polymer particles in concentrated electrolyte solutions merits a separate discussion. The presence of the electrokinetic potential in dispersions with a high electrolyte content requires a new approach to the treatment of the mechanism of the formation of the electrical double layer. At the present time, there exist several hypotheses.[76,87] In the presence of ionogenic surfactants, the increase in the electrophoretic mobility of particles with increase in the electrolyte concentration can be associated, as stated above, with increase in the surface charge density as a consequence of the adsorption of the surfactant.[18,81,88] Presumably the potential around a charged particle in concentrated electrolyte solutions will oscillate and its dependence on concentration will therefore have a complex non-monotonic character.

On the basis of ideas concerning the disruption of the solvate layer by electrolytes, presumably an increase in the electrolyte concentration entails a shift of the slip plane, separating the stationary and mobile parts of the double layer, towards the interface.[89] It has been suggested that the solvate layer is disrupted faster with increasing electrolyte concentrations than the diffuse layer is compressed.

Allowance for the different solvent powers of the solvate layer in relation to anions and cations demonstrated the possibility of increasing the potential of the solvated particles in concentrated electrolyte solutions and the appearance of an electrostatic stability factor of a new type.[90] Studies on these lines are important both for the development of a technology for the deposition of coatings and for the solution of the problem of the stability and generation of the charge on dispersed systems in concentrated electrolyte solutions.

IV. THE STRUCTURE AND PROPERTIES OF METALLOPOLYMER COATINGS

The extensive possibilities for regulating the composition and structure and hence also the properties of metallopolymers permit their use as effective anticorrosion, antifriction, and electrically conducting coatings. The advantages of anticorrosion metallopolymer coatings over polymer coatings arise from the fact that the protective properties of polymers are supplemented by the protective or inhibiting effect of the corresponding metals. The strength and stability of the metallopolymer coatings are as a rule higher than those of

the polymer coatings. Two-layer protective-decorative coatings can be obtained from electrically conducting metallopolymer compositions by electrodeposition.

Metallopolymer coatings are multicomponent systems containing a mixture of oligomers and polymers together with colloidal particles of metals and alloys. Their electrophoretic-electrochemical codeposition on the electrode is in essence the first stage in the formation of the coating. The properties of the composite metallopolymer material formed under these conditions are determined to a large extent by its subsequent hardening at elevated temperatures and mainly by the interactions between the polymeric components and the surface of the metal particles. The segregation of the metal particles, which have an active surface, together with the polymer promotes an increase in the fraction of chemisorption bonds in the system. The nature of the polymer and the type and number of functional groups play the main role in this process.

As a result of the thermal interaction of the oligomers and polymers with the surfaces of colloidal metallic particles, various surface compounds with bonds of different types are produced.[15,16] Ionic bonds (polysulphide) or M–O–C bonds of the covalent type (epoxide and polyester oligomers, polyethylhydrosiloxane) are formed in polymers containing groups with locally concentrated charges. Polymers containing tervalent nitrogen, for example, acrylic oligomers [sic], are capable of interacting with the atoms on the surface of the metallic particles with formation of coordinate bonds. If the polymers contain ether, ester, and hydroxy-groups [polyether and phenol-formaldehyde oligomers and poly(vinyl acetate)], then there is a possibility of their interaction with the surface to form dipole–dipole, ion–dipole, and hydrogen bonds.

Studies on processes involving the formation of metallopolymer coatings from mixtures of oligomers and oligomer–polymer mixtures showed that in this case the compatibility and the interaction of the polymeric components play an important role.[15] The most satisfactory physicochemical properties of the coatings are then attained for the ratio of the components which corresponds to the range of their compatibility or the formation of graft copolymers in the system.

The study of the structure and properties of metallopolymer coatings is part of the general problem of the formation of composite polymeric materials containing fillers of different kinds.[15,16,91] The mechanism of the action of fillers consists in the general case in the fact that in their presence adsorption on the surface of solid particles results in the formation of ordered polymer layers, which play the role of crystallisation centres in crystallising polymers, and of regions determining the structure formation in the entire system in amorphous polymers; the capacity of oligomers and monomers for polymerisation is also important.[92,93] According to modern ideas concerning filled polymer systems, the presence of such layers increases the heterogeneity of the system and improves its mechanical properties as a result of the decrease in the energy of cohesion in boundary layers and the possibility of the relaxation of stresses.[94]

Metallopolymer coatings consist of a polymer base in which metallic particles are distributed. Typical structures of composite metallopolymer deposits are illustrated in Fig. 7. Fig. 7*a* represents a coating obtained by the electrophoretic-electrochemical deposition of dispersions of epoxide and polysulphide oligomers and lead on a steel plate (D_c = 9 A m^{-2}, deposition time 120 s). The ratio of the polymer components is 8.5 : 1.5 and the concentration of the metal is 60 wt.%. The bulk of the oligomers exist in the form of globules 500–1000 A in size. The interaction of the polymers with the colloidal metallic particles on the surface of the latter results in the formation of compacted polymer layers (Fig. 7*b*). They are clearly observed after etching the coating in active oxygen (Fig. 7c). The chemisorption interaction and the formation of surface compounds at the metal–polymer boundary have been confirmed by IR spectroscopic studies.[15,16]

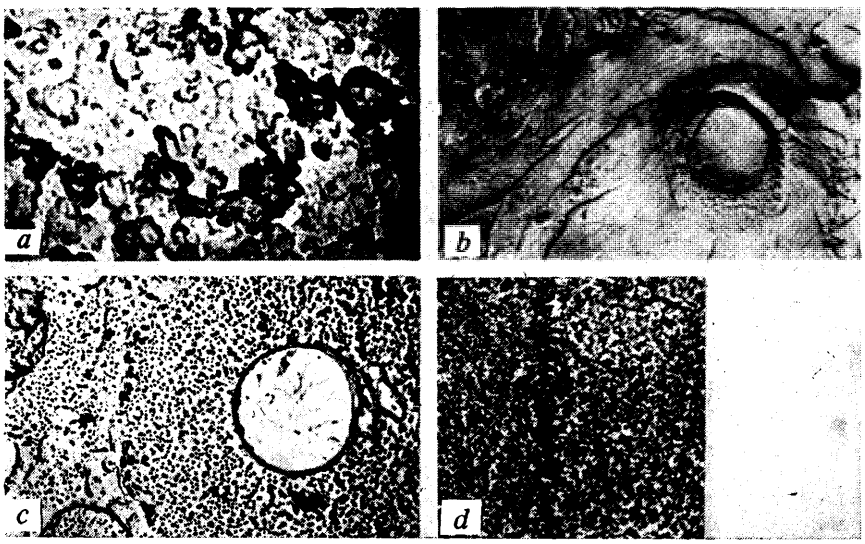


Figure 7. Electron micrographs:[12] *a*) a metallopolymer coating (magnification ×8400); *b*) region near a metallopolymer particle (magnification ×70000); *c*) ditto after etching; *d*) metallopolymer coating on which a profile line has been drawn.

It has been established by X-ray diffraction studies that the partial deformation of the crystal lattice of the metal (for example, reflections characteristic of the β-form of zinc appear) and the change in the packing density of the coatings are a consequence of the chemisorption interaction at high metal concentrations in the metallopolymer coatings.[67]

The formation of interfacial boundary layers of polymers on the surfaces of metallic particles is an important factor, which tends to impart anticorrosion properties to the coatings. Their corrosion stability is associated not only with the inhibiting and protective properties of the metals but also with the hindrance of the access to electrolytes as a consequence of the shielding of the surfaces of the coatings by the surface compounds formed. The degree of perturbation of the corrosion process is then determined by the composition of the coating.

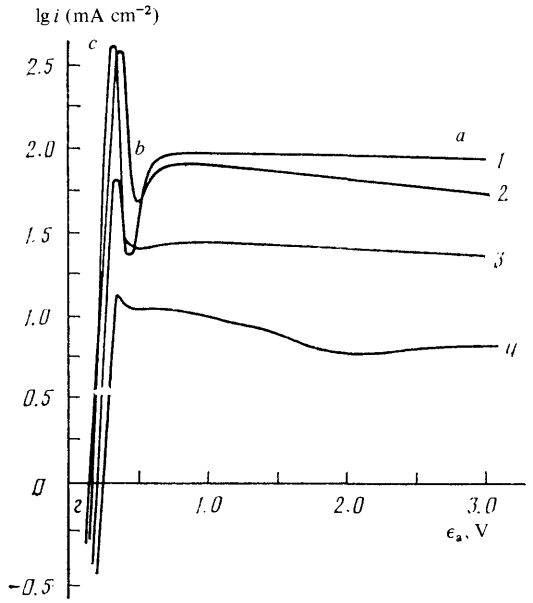


Figure 8. Polarisation curves for the anodic dissolution of copper electrodes in a solution of 200 g litre^{-1} $CuSO_4$ and 90 g litre^{-1} of H_2SO_4: *1*) unprotected electrode; *2)–4)* electrodes with a metallopolymer coating based on an organosilicon oligomer with copper contents of 80, 64, and 44% respectively.[64]

The protective properties of the metallopolymer coatings can be illustrated by comparing the electrochemical behaviour of copper electrodes without a coating and with a metallopolymer coating based on an organosilicon oligomer and copper. Fig. 8 presents the results of a potentiometric study of such electrodes.[64] The metallopolymer coatings were produced by the simultaneous deposition of copper and an emulsion of an organosilicon oligomer (D_C = 7.5 A m^{-2}, τ = 180 s). For small deviations of the equilibrium potential of the electrodes into the anodic region, a sharp rise in the current is observed. After the attainment of certain critical current and potential, the electrodes are passivated. The polarisation curves *1* and *2* are characterised by a maximum and a minimum (points *b* and *c*). The "*ab*" region corresponds to the active dissolution of the metal and the "*cd*" region corresponds to its passive state; the copper dissolution process almost ceases under these conditions. The maximum on the curves is reduced with increasing content of the polymer in the metallopolymer layer and almost disappears for a copper content of 44%, while the passivation potential is reached at lower current densities: at 315.2 mA cm^{-2} for the copper electrode and at 12.6 mA cm^{-2} for the metallopolymer electrode with a copper content of 15%. The rate of corrosion of the copper electrode is 5–6 times greater than that of the metallopolymer coating containing 44% of copper.

The retardation of the dissolution of electrodes with coatings based on oligomers having the COO^-, NH_3^+, $H_2C—CH—$ (O), etc., functional groups is very marked. At lead and copper concentrations in the range 55–68% and zinc and cadmium concentrations in the range 68–73%, the dissolution of the metal ceases almost completely.[12,64] With increase in the metal content in the coating, the shielding of the surface diminishes and, furthermore, the adhesion of the coating to the support is weakened. The conditions for the preparation of metallopolymer coatings based on the above metals and also epoxide and polyether resins as well as organosilicon and polyether varnishes have been described.[12,18,64,70,96]

The metallopolymer coatings with the optimum composition obtained to date have corrosion stabilities superior to those of polymer coatings and the corresponding galvanic coatings (Table 5).

Table 5. The corrosion and mechanical stabilities of polymer, metallic, and metallopolymer coatings.[18]

Composition of coating	Σ, mm	A_1, days	A_2, days
Polymer coating based on E-41 and E-30 epoxide resins	1–2	70	60
Galvanic coating based on lead	—	90	78
Metallopolymer coating based on a mixture of epoxide resins with 60% of lead	1	110	96

Notation: Σ is the bending strength, A_1 the stability in 3% NaCl solution, and A_2 the stability in a chamber with 100% humidity.

The corrosion stability of metallopolymer coatings is greater the stronger the bond between the functional groups of the oligomer and the metal, for example, zinc.[74] It has been noted[95] that, when phenol-formaldehyde oligomers are used, the region of the maximum stability in corrosive media shifts towards higher metal concentrations as the bond between the polymer and the metal weakens in the sequence inner complex (chelate) > ionic > coordinate (via amino-groups) > donor–acceptor (via the OH group) > no chemical bond (ester group). The decrease in the number of epoxide rings on formation of metallopolymer coatings based on epoxide oligomers and the Zn–Pb alloy is accompanied by a sharp fall of corrosion stability.[18,98]

The dependence of the corrosion stability of coatings based on phenol-formaldehyde oligomers and zinc on their content of carboxy-groups passes through an extremum.[74,97,99] This is associated with the fact that, in the region of maximum corrosion stability of the coatings, the concentration of

the functional groups corresponds to the most favourable combination of two mechanisms of protection: the protective mechanism and the insulating mechanism involving the formation of surface compounds.

The introduction of colloidal metals into polymer coatings makes it possible to improve considerably the physicomechanical properties (to increase the adhesion and impact strength) and antifriction properties (to decrease the coefficient of friction and the wear of the material).[15] The thermal and electrical conductivities of metallopolymer coatings can be regulated within wide limits by varying the concentrations of the metals.

The electrical conductivity and the enhanced corrosion stability of metallopolymer materials permit their use as anticorrosion layers (primer) on which polymer compositions or industrial paints, for example, VAS-1162 and EP-2100, are subsequently electrodeposited. Data typical for two-layer metallopolymer–polymer coatings are presented in Table 6 for two industrially manufactured materials (VAS-1162 and EP-2100) with metallopolymer anticorrosion layers (primers) based on lead and the lead–copper alloy. The stability of such a system comprising two-layer coatings during their tests in chambers with 100% humidity and a 5% salt mist is higher by a factor of 2–3 than that of the single-layer industrial coatings of the same thickness (Table 6).

Table 6. The corrosion stabilities of polymer and metallopolymer coatings in a chamber with a 5% salt mist (NaCl)*.[98]

Composition of coating		τ, h
layer II	layer I	
Industrial materials: VAS-1162	—	176
EP-2100	—	176
Lead-based (60 wt.%) metallopolymer primer	VAS-1162	520
	EP-2100	520
Metallopolymer primer based on a lead–copper alloy (60%)	VAS-1162	>615
	EP2100	>615

*The thickness of the coatings was 45 μm.

Table 7. Dependence of the dielectric strength of polymer and two-layer metallopolymer-polymer coatings on the deposition time.[59]

Type of coating	Dielectrical strength (kV) for different deposition times (min)					
	0.5	1.0	1.5	2.0	2.5	3.0
Polymer coating based on a mixture of the E-30 and E-41 epoxide resins	0.8	1.5	1.75	2.0	1.8	1.4
Two-layer coating (first layer—metallopolymer based on a mixture of resins and lead; second layer—mixture of epoxide resins).	2.0	2.7	3.2	3.5	3.7	3.8

An important application of two-layer metallopolymer-polymer coatings involves the creation of highly effective electrically insulating coatings. The results of tests of the electrical strength of polymer and metallopolymer-polymer coatings are presented in Table 7. For the same thickness (40 μm), the dielectric strength of composite two-layer coatings is increased by a factor of two.[12,59] The presence of the metallopolymer layer ensures an increase in adhesion to the support and hence an improvement in the anticorrosion properties and also in the homogeneity, uniformity, and the specified thickness of the coatings along the edges of the given articles.

The electrically insulating properties of the two-layer coatings do not change after periodic alternation of the polarity of the electric field.

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Thus the simultaneous use of two classical phenomena—electrophoresis and electrolysis—had led to the development of new methods of formation of metallopolymer structures and materials. The possibility of regulating the kinetics of electrode processes with the aid of the electrophoretic deposition of polymers–electrophoretic polarisation—is of considerable interest from the standpoint of the electrochemical preparation of metallic powders and the anodic passivation of metals.

Further development of this field requires the solution of a number of problems in colloid chemistry, electrochemistry, and the physical chemistry of filled polymers, which include the problems of the stability of dispersed systems in electric fields, of the electrocrystallisation of metals in polymers, and of the interaction of polymers with colloidal metals.

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Trends in the Development and Tasks of Modern Quantum Chemistry†

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The main advances are surveyed and the principal trends in the development of modern quantum chemistry are noted. The intensification of the linkage between theoretical and experimental research is emphasised. The tasks in various branches of quantum chemistry of greatest current interest are analysed. The electron clouds and the electronic processes in molecules and solids, intermolecular interaction, intramolecular dynamics, elementary processes in gas and condensed phases, and phenomena determined by the non-adiabatic electronic-nuclear interaction are examined. The tasks associated with the development of a theory of the application of physical research methods in chemistry and also those concerned with the applied quantum chemistry, namely theoretical materials science and quantum molecular biology, are discussed. The role of computer modelling is emphasised and the trends in the development of quantum-chemical methods are briefly analysed.
The bibliography includes 269 references.

CONTENTS

I.	Introduction	97
II.	Electron clouds	98
III.	Dynamics of the motion of nuclei	102
IV.	Non-adiabatic electronic-nuclear interactions	105
V.	Development of theories of the application of physical research methods in chemistry	106
VI.	Applied problems	107
VII.	Development of quantum-chemical methods	108

I. INTRODUCTION

Quantum chemistry was born as the science of the electronic structure and reactions of molecules in the gas phase based on quantum mechanics. At the same time, these quantum-mechanical methods have come to be used to explain spectroscopic and other physical properties of molecules. However, experiment required the theory to explain the structure, properties, and reactions not only of molecules as such but also of substances in the liquid and solid states. Together with quantum mechanics, it became necessary to start using the methods of statistical and mathematical physics and computer mathematics for the solution of these problems. Thus modern quantum chemistry is a broad science located between chemistry and physics whose subject is theoretical study of the structure, properties, and transformations of substances at the atomic-molecular level with the aid of methods of quantum mechanics, statistical physics, computational mathematics, and mathematical physics.

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1. Strengthening of the Linkage between Theory and Experiment

Still comparatively recently, in assessing the contribution of quantum chemistry to chemical sciences it was pointed out that it explained many chemical phenomena and regular features, created the system of concepts and the language of modern chemistry, and imparted a physical significance to the existing chemical ideas. These were indeed major advances. However, the success and the role of present-day quantum chemistry are much greater. It is able not only to explain but also to predict the possibility of the existence of new chemical compounds and materials and their structure and properties, as well as new effects, and to calculate the characteristic parameters of molecules which are inaccessible to experiment or can be determined experimentally with difficulty. Quantum chemistry proved able to solve also more complex problems: to recommend, for example, the optimum synthesis of a new compound with specified properties, to indicate how one can measure, in principle, any characteristic parameter or property, and to assist in planning a new experiment. Problems which are ultimately very relevant to practical applications, to the creation of the new engineering, are being solved with increasing frequency. All this characterises the new stage in the development of quantum chemistry. Its role in modern chemistry has changed significantly.

Thus one of the main trends in the development of modern quantum chemistry is strengthening of the linkage with experiment. Whereas 20–30 years ago, the bulk of the literature on quantum chemistry was devoted to methodological developments and trial calculations, nowadays most of the theoretical studies are associated with a specific experiment, with its interpretation, or with predictions. This is due to several causes. On the one hand, quantum-chemical methods have been greatly improved, having reached a level of development where they can really satisfy many of the requirements of experimenters. There has been enormous growth in the power of modern computer techniques. The application of methods of mathematical physics, which make it possible to find solutions to quantum-chemical problems in a closed form or to bring them to the stage where it is rational to resort to computers, has become more effective. The application of methods of statistical physics has been expanded, which gave rise to the possibility of obtaining results in a form which can be compared directly with experiment.

On the other hand, the above tendency is associated with colossal progress in physical experimental methods and their application in chemistry. However, the application of new physical research methods in chemistry is based on special theoretical developments. Quantum chemistry has been concerned to an increasing extent with the solution of this problem.

The increasing role of physical research methods in chemistry led to an enhancement of interest by quantum chemists in the physical properties of molecules. The existence of this trend is already evident from the following example: at the Vth International Congress on Quantum Chemistry in 1985 (Canada), among the new reports delivered by invitation, whose selection is usually made on the basis of a sober assessment of what is new, about 60% were devoted to physical problems important for chemistry and the remaining 40% were concerned with chemical tasks and problems significant for both chemistry and physics (methodological studies).

The main cause of the strengthening of the linkage between quantum chemistry and experiment is ultimately determined by practical requirements: new experiments and new experimental methods are essential for the solution of problems of practical importance. A theory applied to chemistry, namely quantum chemistry, must provide a basis for such experiments and methods and an interpretation of the results.

A vital task for theoreticians is to carry out investigations in close contact with experimenters. In practice this has by no means always been achieved, but it is known that the joint investigations by theoreticians and experimenters always greatly assist in the successful outcome of research.

The Figure presents a schematic illustration of the structure of modern quantum chemistry. Quantum mechanics has made the main contribution to the development of its methods. Statistical physics, computer mathematics, and mathematical physics also play a significant role. Quantum-chemical investigations based on the adiabatic approximation are divided into two fields: the study of electron clouds and the study of the motion of atomic nuclei. The first includes the electronic structure and electronic processes in molecules and solids and intermolecular interaction. The second field embraces the intramolecular dynamics of nuclei, the elementary processes in the gas phase, and the dynamics of the processes in condensed phases and at interfaces. It is known that there exist many systems and phenomena to the description of which the adiabatic approximation is inapplicable and account must be taken of non-adiabatic electronic-nuclear interaction. A separate bunch of quantum chemistry is devoted to such systems.

The development of theories of the application of physical research methods to chemistry, which is related to the fields mentioned above, is a very important component of quantum chemistry. The solution of applied problems is a comparatively new branch of quantum chemistry, which, however, is of very great current importance. In particular it embraces the large field of materials science. Many applied problems are being solved successfully with the aid of computer modelling. One of the most important problems of this kind involves the development of quantum molecular biology.

Some of the most important problems of modern quantum chemistry, in each of the fields mentioned above, are characterised briefly below. The examples quoted are illustrative. In conclusion, the general trends in the development of quantum chemical methods are briefly analysed.

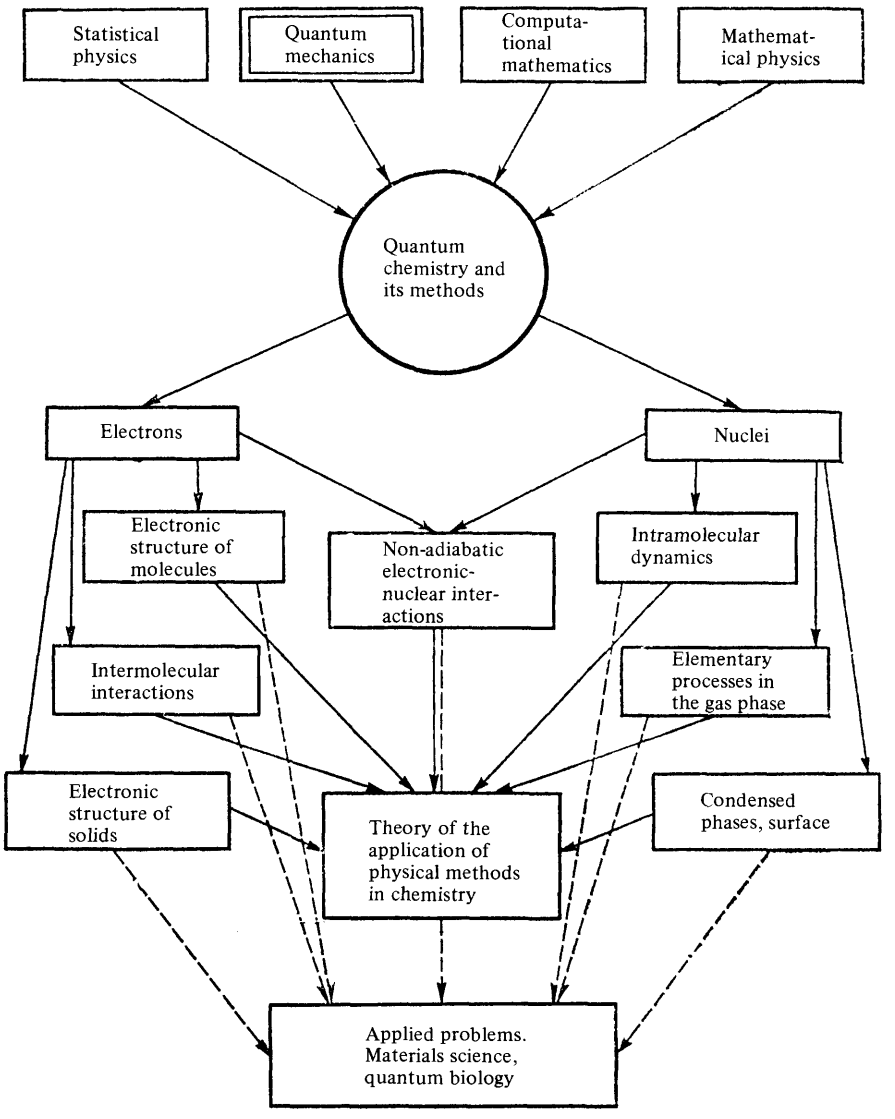
II. ELECTRON CLOUDS

1. Electron Clouds of Molecules

One of the quantum-chemical problems of greatest current importance involves the establishment of a relation between the properties of molecules and their electronic structure. The most important chemical property of molecules is their reactivity. An enormous amount of experimental data, characterising the relation between the reactivity and the electronic structure of molecules has accumulated in this field. There have been major advances also in the theoretical treatment, such as, for example, the principle of the conservation of orbital symmetry of Hoffmann and Woodward,[1] the concept of frontier orbitals,[2–4] and the principle of isolobal analogy.[5,6] The principal trend in the development of the modern theory of reactivity involves an increase in the number and improvement in the quality of calculations of the potential energy surfaces (PES) of reacting systems. Quantum-chemical calculations of the transition states (the saddle point on the PES) and calculations of the directions of motion of atomic nuclei in the given molecular configuration make it possible to predict the reaction path and the nature of the

final products. Hundreds of PES have been calculated[7-14] and the mechanisms of many reactions have been determined with a high degree of probability, which has made it possible to estimate the kinetic parameters necessary for the calculation of their rates. This branch of the theory of reactivity has been very fruitful and in the immediate future will probably influence significantly synthetic chemistry (mainly organic chemistry).

On the other hand, many problems of chemical reactivity have been solved at an empirical level without theoretical justification or have not been solved at all. Thus various empirical rules of different kinds, many of which lack theoretical justification and the limits of the applicability of which are not known, are widely used in organic chemistry. As regards the reactivity of molecules, quantum chemists are therefore faced by a broad field of activity which is of great interest to experimenters. We shall indicate several questions which await an answer. For example, how can one justify the Brønsted–Polanyi–Semenov rule and to what factors are the observed deviations from this rule related:[15] when does the nucleophilic substitution reaction proceed via the S_N2 mechanism and when does it involve the formation of a radical-ion; why do some reactions proceed in general via a concerted mechanism, while others involve intermediate stages; in what cases are metastable intermediate complexes formed; what is the influence of low-lying electronically



The structure of modern quantum chemistry.

excited states on the rates of reaction; how can one increase the selectivity of chemical reactions, i.e. how can one avoid their occurrence via a multiplicity of channels leading to the formation of side products and greatly complicating the manufacturing process and increasing its cost. (We may note that, for certain types of major chemical manufacturing processes, an increase in the yield of product by 2–3% would result in an annual saving equivalent to the cost of construction of a new large factory!)

Various approaches can be usefully resorted to for the solution of numerous problems of the theory of the reactivity of chemical compounds. Together with the calculations of the PES mentioned above, semiquantitative approaches are of interest for specific reactions:[7–14] the construction of semiempirical PES[10] or the estimation of diabatic terms modelling certain cross-sections through the PES for the reacting system.[15] Calculations of the electronic structure and properties of the intermediate formations, which are not susceptible or are little susceptible to experimental study, are also important.

It is noteworthy that, as a result of the improvement of experimental techniques, many chemical reactions known previously only in solutions have now been investigated also in the gas phase;[16,17] this makes possible the comparison of the results of the calculation of reactivity with the "pure" experiment.

There are many problems in the theory of electronic structure which are not related directly to reactivity but are important for chemistry. They include, for example, the development and application of the model of "additional spherical electron density",[18] which justifies the Lewis–Sidgwick rule. According to this rule, electronic configurations resembling those in inert gas atoms are especially stable in coordination compounds. Calculations of the electronic structure of compounds with heavy atoms taking into account relativistic effects are very important. It is now clear that, without taking the latter into account, it is impossible to explain satisfactorily either the chemical or physical properties of compounds of the actinides, lanthanides, and other elements with a high anionic number.[19,20] Many characteristic features of compounds with heavy atoms are influenced, in a manner which is not yet fully understood, by the presence in these atoms of a large number of closely spaced energy levels.[20–23] In general, the theory of chemical bonding involving the atoms of heavy elements still has to be constructed. The nature of the metal–metal bonds,[24,25] the structure of compounds involving variable-valence metal atoms,[26] and many others have to be investigated.

Among the physical methods for the study of matter, the most important information about the electronic structure of molecules is provided by spectroscopic methods: spectroscopy in the visible, ultraviolet, and X-ray regions, X-ray and photoelectron spectroscopy, Auger spectroscopy, EPR, and NQR. The task of quantum chemistry is primarily a correct interpretation of the wide variety of information obtained by these methods: data on the energies of electronic transitions, the form, intensity, and polarisation of electronic, vibronic, and rovibronic spectra, their fine structure, their behaviour in external fields, and many others. Calculations of the energies of excited electronic states as a function of nuclear coordinates (PES) are of special interest. The modern quantum-chemical methods so far permit the calculation with an adequate accuracy of the structure and spectra only of small molecules.[14,21] However, their characteristics are important for the solution of many practical problems.

The development of laser techniques during the last decade has allowed the investigation of many fast chemical, physical, and biophysical processes on the nanosecond and picosecond time scales. The development of the appropriate theories is essential for the interpretation of these experiments. Theoretical study of the rates of the transfer and capture of the electronic excitation energy of molecules, calculations of the lifetimes of excited states in relation to radiative and non-radiative decompositions, and the study of the pathways and rates of relaxation processes are of special interest: the calculations of the ionisation, autoionisation, and dissociation cross-sections of molecules and the cross-sections of their excitation and superexcitation by single-photon and multiphoton irradiation and other types of ionising radiation, the cross-sections of the resonance and non-resonance light scattering, etc. are also important. The solution of these problems, which characterise the leading front of present day science of the interaction of radiation with electron clouds, is necessary for the construction of a theory of elementary reactions, the development of theories of vibronic interactions, the usual and laser photochemistry, radiation chemistry, and plasma chemistry, for the calculation of the conditions governing the operation of molecular, excimer, and chemical lasers, etc.[27–34]

The modern spectroscopic methods are characterised by a high resolving power and a high sensitivity. This imposes enhanced requirements on quantum-chemical calculations. It is important to be able to calculate fine effects for the understanding of which it is necessary to resort to the entire range of procedures of modern theoretical physics. The high sensitivity of modern spectroscopic instruments has made it possible to observe a series of previously unknown or little investigated metastable species, the nature, structure, and properties of which have to be studied jointly by experimenters and quantum chemists. Such species have been detected in gas-phase chemical reactions, electrical discharges, and by the action of strong electromagnetic fields and ionising radiation in plasma, space, etc.

2. Intermolecular Interactions

The theory of intermolecular interactions has always attracted the attention of scientists because of the role which such interactions play in various physicochemical phenomena in both gaseous and (especially) condensed media.[35] During the last 10–15 years, the theoretical research in this field has advanced appreciably in connection with the creation and development of a series of new effective experimental methods for the investigation of the interaction of molecules in the gas phase.[36] These studies yielded extensive new information about the intermolecular interaction, which, on the one hand, required theoretical interpretation and, on the other, served as a basis for checking calculations.

The main task of the theory of intermolecular interaction involves the study of potential energy surfaces in both ground and electronically excited states. The relevant information can be obtained experimentally only in the simplest one-dimensional cases, mainly for the ground electronic states. For problems associated with the study of the physical properties of molecular complexes, liquids, solutions, and clusters, it is in many cases sufficient to know the PES in the vicinity of the equilibrium position for the ground electronic state. For the theory of elementary processes, especially chemical and photochemical ones, the theory of chemical laser systems, and the solution of many other problems, it is essential to know the changes in potential energy over a wide range of variation of nuclear coordinates for both ground and electronically excited and ionised states taking into account the possibility of the existence of several reaction channels.[7–14]

The study of the effect of the molecules of the medium (the solvent) on the rate of the chemical reaction constitutes an independent problem. Disregarding the questions concerning the dynamic action of the medium (see subsection 3 of Section III), the solution of this problem reduces to the calculation of a multidimensional PES taking into account the molecules of the medium. Model calculations have made it possible in a number of instances to take this phenomenon into account qualitatively.[7,37] Here the natural question arises what number of solvent molecules must be taken into account. At first sight it may turn out that this number should be very great, especially when the reacting system is charged, since Coulombic forces decrease slowly with distance. However, recent experiments involving the study of the multistage solvation of ions in the gas phase have shown that the nearest ligands play the main role in this process and that the influence of more remote ones may be neglected.[16,17] The qualitative difference between gaseous and solvated systems is determined in many instances by the action of only a single ligand. Hence it apparently follows that, in theoretical estimates of solvation effects in both thermodynamic and kinetic problems, the treatment can be restricted in most cases to clusters comprising a small number (6–8) of ligands. A model calculation of the potential energy curve for proton transfer in the $FH...NH_3$ system shows that for the gas phase this curve has only one minimum while for the solution, when account is taken of the hydration shell of this complex consisting of six water molecules, a second fairly deep minimum appears.[38] The question of the influence of solvation on elementary processes requires thorough investigation.

In certain cases interesting conclusions concerning the influence of intermolecular interaction on the rate of reaction can be reached without any calculation. For example, the reaction $Cl_2 + Br_2 \rightarrow 2ClBr$ is known to be symmetry-prohibited (it requires a high activation energy[1]). However, the same reaction involving the van der Waals complex $(Cl_2)_2$ takes place readily, since the symmetry prohibition has been removed.[39] Application of the orbital symmetry conservation rules to reactions involving van der Waals complexes may prove useful also in other cases.

It has been frequently suggested that the form of the activated complex for a bimolecular reaction resembles that of the corresponding stable molecular complex. Such similarity would be important because the form of the latter complex can be determined experimentally. However, it has been found that in general no such similarity exists.[39] The problem of the theoretical analysis of the conditions under which it can nevertheless occur therefore arises.

An important task of the theory is also the study of the changes in various characteristic parameters and properties of molecules under the influence of their interaction: on formation of molecular complexes, especially hydrogen-bonded complexes, in solvation, adsorption, etc.[36,40]

An increasing amount of experimental data, indicating the important role of cooperative (multispecies) interactions of molecules in condensed phases, has accumulated in recent years.[36,41,42] Such interactions are manifested by the nonadditivity of the interaction energy and the sharp changes in vibrational spectra, equilibrium geometry, and other characteristics of the molecules on passing from a dimer to an aggregate. The theory of the cooperative interactions of molecules is as yet far from being complete.

3. The Electronic Structure of Solids

During the last two decades, the theory of the solid state has developed vigorously. We shall not be concerned with the general problems of the solid state physics and shall characterise briefly only some of the problems of the theory of the electronic structure of solids relevant to chemistry. These include in the first place problems associated with the properties of the surface.

The creation in the 1970's of a series of new extremely effective methods for the experimental investigations of the surface led to an unprecedented advance in theoretical research into the electronic structure and properties of the surfaces of solids and interfaces. Among the new methods designed to investigate the composition, geometry, and electronic structure of surfaces, mention should be made of slow electron diffraction, photoemission,[43] the spectroscopy of energy losses by electrons,[44] photoelectron and X-ray electronic spectroscopy,[45–47] etc. In connection with the development of these methods, many specific theoretical problems, whose formulation would have been premature in the absence of these methods, have arisen.

One such problem involved the determination of the difference between the electronic structures and the arrangements of atoms in the surface layer and in the bulk of a crystal and also the elucidation of the way in which these characteristics change under the influence of adsorption and local defects. It is also important to know how adsorbed molecules and defects influence the position of the local energy levels, the density of states, the form of the photoemission spectrum, etc.[43]

In connection with one of the most important problems in chemistry, that of heterogeneous catalysis, numerous tasks involving the theoretical study of the adsorption of molecules, molecular fragments, and various intermediate complexes on the active centres of catalysts have arisen.[48–50] Analogous calculations are also necessary for the theory of metal complex catalysis.[51–53] The accumulation of calculated data on the steric orientation of the adsorbed molecules and the nature of their bond with the active centre, the relative adsorption energies of different species on different centres with different types of orientation, the rearrangement of the surface in adsorption, and the interaction of adsorbed molecules is very important. In particular, such calculations can assist in the search for the optimum catalytic reaction pathway. Calculations of the characteristic parameters of adsorbed molecules and other species, namely the frequencies of the electronic and vibrational transitions, dipole moments, and distribution of electron density, as well as various NMR and EPR parameters, are also important for the interpretation of data obtained by physical research methods.[54]

The study of the electronic structure not only of the surface but also of the bulk of the solid, i.e. the local states and defects in the bulk phase, their excitations, ionisation, tunnel recombination, autoionisation, luminescence, etc., is likewise of interest for chemistry.[52,55,56]

The development of the theory of electronic structure and electronic processes in organic crystals with a quasi-one-dimensional structure constitutes a separate problem.[57,58] In a number of instances such structures, which include, in particular, oriented polymers with conjugated bonds,[59] have completely unusual dielectric, conducting, and magnetic properties.

Methodologically, one of the main trends in the development of the theory of the electronic structure of solids is the endeavour to transfer to this theory the methods and approaches developed in the theory of the electronic structure of molecules. This applies in the first place to the treatment of the properties which are determined to a significant extent by the short-range order and local characteristics of the structure—point defects in the bulk phase and on the surface, the presence of adsorbed atoms and molecules, optical and X-ray excitations, etc. The joint application of the methods of the theories of molecular and

solid state structures will undoubtedly prove useful in the treatment of the properties of non-crystalline solids and alloys, the stability of materials with respect to the action of radiation, corrosion, etc. The cluster model, within the framework of which the methods of the theory of the electronic structure of molecules are also applied, has been used successfully in the study of these properties.[60,61]

It is noteworthy that in the theory of the electronic structure of solids, as in the theory of molecules, clear models play an important role. For example, the representation of molecular orbitals by a linear combination of atomic orbitals makes it possible to describe many features of the structure and a number of properties of not only molecules but also of solids.[62,63] Further development of clear representations of the electronic structures of solids is therefore useful, especially for experimenters.

III. DYNAMICS OF THE MOTION OF NUCLEI

1. Intramolecular Dynamics of Nuclei

Under the influence of the development and wide-scale application of new physical research methods, the theoretical study of the dynamic properties of substances has greatly intensified. The intramolecular dynamics of nuclei occupies an outstanding place in such research.

Until recently, in the study of intramolecular non-radiative processes most attention was devoted to electronic relaxation. In recent years, the research into the vibrational and rotational relaxation of molecules has grown appreciably, which is directly related to advances in the development of the laser technique. By virtue of these advances, the dynamics of various intramolecular processes,[64-72] including isomerisation, decomposition, tunnelling, relaxation time, etc., have become susceptible to detailed investigation.

The study of the exchange of vibrational energy is of primary interest.[64,70,71] A definite amount of energy, calculated to produce a local excitation of a specific vibrational mode, is imparted with the aid of a laser to a molecule having a very low rotational and vibrational temperature. The creation of such a non-equilibrium distribution under the conditions of a high vacuum can lead to the dissociation of the molecule if the rate of this reaction is higher than the rate of redistribution of the additional energy among other vibrational degrees of freedom, i.e. than the rate of intramolecular vibrational randomisation (stochastisation). The task of the theory is to facilitate with the aid of calculations the search for the selective vibrational excitation of the molecule in which this condition would be fulfilled. Calculations can help to elucidate the causes of the observed deviation from the experimental data of the rates of photoinitiated dissociation calculated on the basis of a statistical model.[73] The deviations can be caused by the incomplete randomisation of the energy, kinematic effects, insufficiently accurate calculations of the PES, etc. Calculations not only of the PES but also of the vibrational energy levels for the ground and electronically excited states, the constants for the anharmonic and kinematic interactions of modes, the probabilities of energy transfer between the modes, etc. are therefore necessary. Questions of this kind are part of the broader problem of the relation between the ergodic and random motions in the molecule, a problem which should be solved by means of the joint efforts of experimenters and theoreticians (see, for example, Noid et al.[74] and Krivoshei et al.[75]).

The problem of the influence of the non-equilibrium distribution of energy on the rate of unimolecular decomposition of molecules does not arise solely in connection with laser excitation. A non-equilibrium distribution can arise for different reasons; in particular, it is created in the course of the reaction itself. It can be neglected only in terms of the rapid mixing (randomisation) approximation. The development of these problems is of very urgent interest for chemical kinetics.[76,77]

A series of theoretical problems in intramolecular nuclear dynamics and as regards the structure of electron clouds are related to the increase in the sensitivity and resolving power of spectroscopic instruments. Thus the improvement of the resolution of the rotational and vibrational-rotational spectra to 10^{-3} cm^{-1} for a line width up to approximately 5×10^{-4} cm^{-1} imposes new requirements on the accuracy of the calculations and interpretation of the spectra.[67,78-80] To characterise the complexity of this problem, we may mention the high-resolution laser IR spectrum of the comparatively simple ion H_3O^+: approximately 100 transitions have been detected for this ion in the region of 3500 cm^{-1} in plasma cooled with liquid nitrogen, whereas in plasma cooled with liquid air an additional ~240 transitions were observed, but these have not as yet been interpreted.[67] The interpretation of such complex spectra requires the development of new computational methods, such as, for example, the method of computer modelling. New approaches have also arisen in the calculations of the force constants of molecules.[81]

The problem of the calculation of the vibrational spectra of non-rigid molecules, in particular molecules with pseudo-rotation,[82,83] molecules with conformational transitions, etc. is also of urgent interest. In the treatment of such spectra, it is necessary to solve the problem of the motion of atomic nuclei in a field with a complex potential.[84,85]

Many new fairly puzzling data concerning the dynamics of strong hydrogen bonds have appeared in recent years. These findings have not as yet been explained satisfactorily within the framework of a single approach. Such phenomena include, for example, various "anomalous" isotope effects for geometrical parameters,[86] the frequencies and intensities of stretching and deformation vibrations,[87,88] etc.

A number of interesting theoretical problems in intramolecular dynamics have arisen in connection with NMR.[89,90] Here information about the character of the motion of nuclei (for example, about their hindered rotation) is extracted with the aid of the theory of the NMR line form.[91]

2. Dynamics of Elementary Processes in the Gas Phase

The main task of the theory of elementary processes in a gas is the elucidation of the mechanisms of these processes and the calculation of the corresponding rate constants. Knowledge of the latter permits the calculation of the rates of complex multistage chemical reactions, the determination of the pathway followed in the degradation of energy and of the rate of such degradation in photochemical processes, calculations for laser gas-phase systems, processes in plasma, ultrasonic flow, etc. The experimental determination of the elementary constants, especially at high temperatures, is frequently difficult. The role of the theory is especially great in this instance. The study of the dynamics of gas-phase reactions is not important solely for practical purposes; investigation of such reactions makes it possible to learn about the mechanisms of the chemical reaction in a "pure" form uncomplicated by the influence of the medium.

As in the theory of molecular structure, theoretical investigations of elementary processes in the gas phase have received a new stimulus during the last decade by experiments using the new technology, in the first place lasers. Here it must

be emphasised that successful experimental studies of chemical reactions became possible by virtue of their combination with theoretical calculations.

The elementary processes, the calculation of the cross-sections of which is urgently necessary, are extremely varied. They include processes involving the transfer of electronic, vibrational, and rotational energy, charge transfer, ionisation, and decomposition, photodissociation, substitution, etc. reactions,[34,92,93] Many processes take place non-adiabatically.[94,95] The tunnel effect sometimes plays an important role.[96] Whereas two decades ago measurements were made mainly of the cross-sections of processes averaged with respect to rates and the quantum numbers of the initial and final species, in recent years the new technology has made it possible to measure cross-sections with a high resolution with respect to energy in molecular beams, the dependence of the cross-sections on the quantum numbers, the distribution of the products with respect to quantum states, etc. New requirements as regards the quality of the theory have therefore arisen. Thus it has become clear that, when the vibrational relaxation of molecules is considered, account must be taken of the change in their rotational state; it is important to take into account the anharmonic and Coriolis interaction of the modes, the occurrence of the van der Waals interaction of molecules which have collided, and the possibility of their chemical reaction.[97-99] Interesting problems arise in the interpretation of the results of the study of the transfer of rotational energy in beams taking into account the changes in the projection of the angular momentum.[100]

One of the new tasks of the theory of elementary processes consists in finding the transverse cross-sections of chemical reactions between species one of which (a molecule) was subjected beforehand to selective vibrational or rotational excitation.[101,102] For example, it is known that the reaction $N_2O + Cu \rightarrow N_2 + CuO$ on the surface of copper under the conditions of the excitation by a laser of the antisymmetric longitudinal vibrational of the N_2O molecule is 5×10^3 times faster than the thermal reaction on the same surface at 363 K.[101] It has been observed that the rates of the $N_2^+ + Ar$ and $H_2^+ + Ar$ reactions are a maximum on excitation of a specific vibrational level in the initial molecule; this maximum is apparently associated with the resonance (still incompletely understood) between the vibrations of the initial and final molecules.[103] Such resonance-induced increase in the rate of reaction has been observed in certain cases also for a specific translational energy of the species which have collided.

It is of interest to interpret theoretically the experimentally observed appearance of two maxima on the curve describing the dependence of the population of the rotational levels of the product molecules on the rotational quantum number of the initial molecule, which apparently indicates the existence of two decisive configurations of the activated complex (for example, in the reaction $MgH_2 \rightarrow MgH + H$).[103] It is also urgently necessary to obtain an answer to the question in what cases does the distribution of energy in the intermediate state become statistical and in what cases is there sufficient time for the reaction to occur before the randomisation of the energy.

A weak point in the theory of elementary processes is the calculation of the PES, which is usually performed with an inadequate accuracy. As regards the dynamics of the process itself, extremely effective methods have been developed for its treatment, which in the presence of a sufficiently accurate PES make it possible to achieve satisfactory estimates of the collision cross-sections. The calculations of cross-sections based on the solution of the Schrödinger equation have been most widely used (see the relevant reviews[92,104-106]). The success of the calculations of the rates of reaction depends to an appreciable extent on the successful choice of the curvilinear coordinates in terms of which the problem is solved.[106,107]

A number of other quantum-chemical methods of the collision theory are in the stage of intense development (see the reviews[108,109]). Together with these methods, trajectory calculations have become fairly common[110-113] in which classical trajectories of the motions of the representative point of the reaction are calculated with the aid of Newton's equation on a specified PES under different initial (quantum) conditions. In order to obtain the rate constant, the flux of particles is averaged over the thermal distribution. Allowance for quantum effects (tunnelling, interference, resonances) requires a more sophisticated calculation. The corresponding method is called semiclassical.[114]

However, it is necessary to recognise that the application of the above methods to systems with more than three atoms involves considerable computational difficulties. The statistical method for the calculation of reaction rates—the transition state method—has therefore come to be widely used. This method requires much less detailed information about the PES than the other methods.

The principal disadvantage of the initial transition state theory[115] was that no account was taken in it of the trajectory of the reverse motion on the PES of the representative points of the reaction towards the initial state, as a result of which the calculated rate constant was overestimated.[116] Furthermore, an insufficiently complete account was taken of tunnelling. A weak point of the theory was also the hypothesis of the separation of coordinates corresponding to different degrees of freedom and the neglect of the anharmonicity of the vibrations in the calculation of the vibrational partition functions. The subsequent development of the theory was directed mainly towards the elimination of these disadvantages.[117-123] As a result, a general transition state theory was developed, the central place in which is occupied by allowance for the trajectories of the reverse motion with the aid of a variational procedure (see the review of Truhlar et al.[124]).

We may note that the transition state theory is not always applicable to reactions in solution, because it does not take into account the stochastic character of the molecular motion (see the following subsection).

3. Dynamics of Elementary Processes in Condensed Phases and at Interfaces

For a long time the influence of the medium on elementary chemical processes in the liquid phase was taken into account in the majority of theoretical studies mainly in terms of the static approximation where only the change in the profile of the reaction path under the influence of the interaction with solvent molecules is taken into consideration.[125,126] The dynamic character of the influence was taken into account inadequately. For example, in the investigation of the kinetics of electron transfer by Marcus no account was taken of the Brownian character of the motion of the system in the formation of the activated state; only the reorganisation of the solvent and its influence on the activation energy were taken into consideration.[125] In a number of other studies, the charge transfer process was treated as non-adiabatic within the framework of a fairly special model.[127,128]

Later two approaches came to be used for the treatment of elementary processes in the liquid phase: the model based on the Brownian character of the motion of the reacting system along the reaction pathway (Kramers[129]) and the generalised Langevin equation.[130] According to the latter, the motion of the representative point in the liquid phase takes place under the influence of a random force in the presence of time-dependent friction. A common feature of these approaches is allowance for the deactivating influence of the collisions of the reacting molecules with the molecules of the medium, which diminishes the rate constant compared with the value calculated from the transition state theory. It has been shown recently that the two approaches are in essence equivalent.[131] An adiabatic theory of charge transfer has been developed within the framework of the Kramers model.[132–137] The generalised Langevin equation combined with the formalism of the time correlation function has found extensive application in the treatment of various reactions (see the relevant reviews[138–142]). Proton transfer processes[143–144] isomerisation reactions,[144–147] atom transfer reactions,[148] etc.[147,149–152] have been investigated. This branch of the theory of liquid phase reactions undoubtedly merits constant attention and development.

One of the fundamental problems in liquid-phase kinetics involved the solution of the problem of the character of the breakdown of the equilibrium distribution of the populations of the energy levels under the influence of the reaction. An experimental solution of this problem has become possible by virtue of the development of the laser technique.[32] It is important to understand how such breakdowns affect the rate and mechanism of the process.

New possibilities for the development of research into elementary processes in the condensed phase have arisen as a result of the application of picosecond and subpicosecond laser spectroscopy[153] and especially the method of laser-induced fluorescence.[154] Comparatively recently it has become possible to measure with the aid of ultrashort light pulses the rate of ultrafast elementary processes with durations in the range 10^{-11}–10^{-15} s.[155–157] Measurements of the characteristic times of the collisions of molecules in the liquid phase, of the redistribution of energy between different degrees of freedom in the excited molecule, of the times required for the dissipation of the excitation energy, of the intermolecular and intramolecular transitions of the electron and protons, of photodissociation, of the redistribution of atoms in the molecular system, etc. have been initiated. The application of this technique has led to a revolution in the study of ultrafast processes and made it possible to achieve a series of exceptionally interesting investigations.[153–156] For example, it has been shown that the rate of the intramolecular transition of an electron is controlled by the molecular motion.[157] This conclusion is based on the observation of proportionality between the relaxation time of the electronic transition and the corrected dielectric relaxation time of the medium. On the basis of results of similar measurements, it is possible to model confidently the corresponding processes.

Definite progress in the theory of liquid-phase reactions may be expected in connection with the application of the methods of molecular dynamics and in general of computer modelling, naturally subject to a sufficiently realistic approximation of the PES.[158–160] These methods have been used successfully in the study of not only elementary processes but also of molecular spectra.[158–160] We may note, however, that the dynamic effect of the liquid medium on the form and width of the bands in the rotational and vibrational spectra of molecules[161–163] and also in the EPR and NMR spectra[164,165] has already been successfully investigated for a long time on the basis of model approaches with the aid of methods of theoretical physics.

The computer modelling methods have found applications also in the study of the structure and dynamic properties of solids.[166]

One of the most important problems in quantum chemistry involves the study of the dynamics of elementary processes on the surfaces of solids.[167–170] It has already been demonstrated comparatively recently that the atoms distributed on the surface cannot as a rule be regarded as immobile when gas-phase molecules collide with them. However, the number of degrees of freedom which must then be taken into account is much greater than in calculations on the collisions of molecules with one another. Therefore theoretical study of the collisions of molecules with the surface has become appreciably more complicated. The first problem which arises here involves, as for a liquid medium, the determination of the minimum number of molecules which must be explicitly taken into account in the calculations on elementary processes on the surface. It is then necessary to find the PES. The main difficulty in the treatment of processes involving the collision of molecules with the surface is the inapplicability of the standard Born distorted wave method because the interactions are strong and the velocities of the molecules are low. Furthermore, a number of problems are associated with the need to take account of a large number of interacting reaction channels; it is difficult to take into account the quantum effects, especially for light atoms (interference, tunnelling), and also the energy exchange between molecules and phonons both in the bulk phase and on the surface. Nevertheless, many dynamic problems of the interaction of gas species with the surface of a solid have been solved successfully.[167–171] For example, the dynamics of the adsorption of diatomic ions on the surface of a metal, the reactions of oxygen atoms with the surface of carbon-containing platinum,[172] the dynamics of the recombination of hydrogen atoms on tungsten,[173] the adsorption of atoms taking into account relaxation processes,[174–178] the dynamics of adsorption in the presence of interaction with phonons,[179,180] the migration of atoms along the surface,[181] and other processes have been investigated.

A number of interesting problems in the dynamics of surface processes arise in connection with the development of new research methods. Among the latter, mention may be made of the molecular beam method,[167] desorption with angular resolution stimulated by electrons and phonons,[182] the spectroscopy of the energy losses by the electrons scattered by the surface,[44,183] Raman spectroscopy,[184] and other methods.

The promising nature of the method of the laser-induced fluorescence,[154] which provides unique detailed information about the distribution of energy in different stages of the reaction, in particular, for a reaction on the surface and in desorption, about the concentration and nature of radicals appearing in heterogeneous catalysis, and about other processes, which is extremely important under experimental conditions when other spectroscopic methods are inapplicable, must be specially emphasised. Such information should play a primary role both in the formulation of the theoretical problem of the dynamics of surface phenomena and in comparing the theory with experiment. We may note that the generalised Langevin equation has been used with some success for the description of the dynamics of the surface–gas system.[167,172,185]

The study of the dynamics of elementary processes plays an important role in the theory of catalysis (see, for example, Kiselev and Krylov,[186] Chapter 5). Here the initial problem is to discover the elementary stages comprising the catalytic process. It is known that even seemingly simple reactions, for example the catalytic synthesis of methanol,[187] involve a large number of intermediate stages. Theoreticians can assist in the analysis of reactions of this type by studying not only the PES but also the dynamics of individual stages. However, calculations for

only the simplest processes are in fact possible at the present time. Some of these were mentioned above.

In addition, it is useful to involve quantum chemists in the solution of fundamental interrelated problems of catalysis: concerning the mechanism of the decrease in the activation energy and of the change in the reaction pathway under the influence of catalysts and also in seeking an answer to the most important question how to avoid multichannel occurrence in catalytic reactions and how to reduce the amount of side products. Enzyme catalysis is known to be an example of high selectivity (see, for example, Refs.188–190). A high selectivity of the reaction implies that it is faster along one channel than along another. This optimum reaction pathway is probably associated with the self-organisation of the system, which presumably reduces to the choice of the most "favourable" sequence of stages and the optimum mutual orientation of the components of the reacting system in combination with the optimum character of their activation at each stage of the process. The natural question arises why these conditions are fulfilled in enzyme catalysis with such unvarying rigour. For this reason, modelling, especially computer modelling, of the possible mechanisms of the catalytic action of enzymes (and also of ordinary catalysts) constitutes an important task in quantum chemistry.

When the temperature is sharply reduced, the rates of many chemical reactions in the solid state are known to decrease initially in accordance with the Arrhenius law after which they cease to depend on temperature and the reaction proceeds at a low rate, which, however, is higher than the rate corresponding to the Arrhenius equation at the given temperature.[191,192] The existence of this low-temperature limit has been explained by Gol'danskii[192] by a tunnel reaction mechanism. However, the problem cannot be regarded as entirely elucidated. Its solution requires calculations for specific models. For example, Bazilevskii and co-workers[193,194] proposed a model for the ionic polymerisation reaction in crystalline formaldehyde in which the polymer chain propagation stage, which determines the rate of the entire process, takes place with a "favourable" mutual orientation of the molecules and involves very slight atomic displacements. If the height of the corresponding potential barrier is then fairly small, the atomic displacements can in general occur via both the tunnel mechanism and over the barrier. At a low temperature, the rate of reaction can then be determined both by the low tunnelling probability and by the low probability of the realisation of the "favourable" orientation of the molecules. In the absence of a barrier, only the second cause will naturally operate. At the usual temperatures, the reaction proceeds via another (activated) pathway, since the latter is faster. Fairly correct calculations have been performed for hydrogen transfer reactions[195] and the quantum nature of the low-temperature limit of the reaction rate has been demonstrated (see also Refs.72, 123, and 196).

IV. NON-ADIABATIC ELECTRONIC-NUCLEAR INTERACTIONS

It is known that the behaviour and properties of atomic-molecular systems can be largely treated in terms of the adiabatic approximation. However, under certain conditions the adiabatic separation of the electronic and nuclear motions is illegitimate. Studies in recent years have shown that in any molecular system there is a possibility of a situation where it is essential to take into account the non-adiabatic electronic-nuclear interaction, i.e. the situation where the electrons and nuclei must be regarded as a single dynamic system.

The interaction of nuclei and electrons is manifested in different ways for bound and unbound states. In the former case, the interaction is referred to as vibronic. It can be disregarded if the characteristic vibration frequency ν_{vibr} is much lower than the frequency ν_{el} corresponding to the electronic transition between the ground and first excited states. The limiting situation, which infringes this condition, occurs when the electronic energy states are degenerate ($\nu_{el} = 0$) in a certain region or at one point in space. If the degeneracy is associated with the symmetry of the system, then, according to the Jahn–Teller theorem, the symmetrical configuration of the nuclei proves to be unstable because of the mixing of the electronic states by nuclear displacements. Depending on the nature of the degeneracy, two or more distorted configurations will be stable. Such manifestation of the vibronic interaction is referred to as the Jahn–Teller effect.[197,198]

Thus, in the situation indicated, the Jahn–Teller effect actually determines the real structure of the molecular system and also its dynamics and certain physical and chemical properties which depend on the structure. During the last 20 years, manifestations of the Jahn–Teller effect have been observed in many compounds with the aid of various experimental methods: EPR, IR, Raman, and UV spectroscopy, photoelectron spectroscopy, and studies of the polarisability and magnetic susceptibility of substances. The Jahn–Teller effect is significant in crystal chemistry and influences structural phase transitions (the cooperative Jahn–Teller effect), especially the transitions associated with the spontaneous polarisation of crystals (ferroelectric phase transition). The theory explains satisfactorily the observed effects and has been used successfully in many instances for prediction.[197–202] A model of the fusion of solids has been recently proposed[203] on the basis of the Jahn–Teller effect.

The vibronic interaction is manifested also in those cases where ν_{el} is non-zero but is of the same order of magnitude as ν_{vibr}.[197,198] The corresponding effect is frequently referred to as the pseudo-Jahn–Teller effect. This situation is frequently encountered, for example, in molecules which are in highly excited electronic Rydberg states[199] and in compounds with transition metals.[21–23,26] Thus, in the energy range from 0 to 0.54 eV, the iron molecule $Fe_2(^7\Delta_u)$ has 112 electronic states.

With the aid of the pseudo-Jahn–Teller effect, it is possible to explain in many instances the shape of the molecule—for example, the stability of the planar form of the ammonia or methane molecule.[204] It is also noteworthy that the mathematical formulation of a theory of this effect helped to justify and extend the Woodward–Hoffmann orbital symmetry conservation rules.[205] Furthermore, it is also possible to obtain other useful results of a qualitative character; for example, one can explain the characteristics of the mutual influence of ligands, the relative stabilities of the isomers of coordination compounds, the geometrical features of metalloporphyrin molecules, etc.[204] In certain cases, recommendations concerning the formulation of the experiment in order to observe a new phenomenon follow from the theory.

The main task in the future application of the vibronic inter action theory lies apparently in the field of chemical reactions. It may be hoped that the existing theory will permit a deeper understanding of the mechanisms of elementary chemical reactions. The applications of the theory to the solution of certain problems in materials science (see below), in the theory of structural phase transitions, and in other applied problems, may prove very useful. At the same time, it is important to improve the theory itself: to learn to perform calculations correctly in the presence of a large number of

closely spaced states, in the presence of the spin–orbit interaction, etc.[22,23,206]

The manifestation of non-adiabatic conditions for unbound states, for example, in collisions between molecules, consist in the fact that, under its influence, any regular system can under certain conditions undergo a non-radiative transition with a finite probability from one electronic energy state to another having the same symmetry. For this, it is essential that the nuclei (the "slow" subsystem) should fall within the region of the configuration space where these energy states are at fairly short distances from one another and the rate at which the nuclei move is not too low. This effect plays a primary role in non-radiative transitions, in electronic relaxation, in the theory of non-elastic and reactive collisions, etc.[29,34,94,95,207] Situations are encountered in which non-adiabatic transitions occur between vibronic energy states, and not simply between electronic states, under the influence of a strong vibronic interaction.[99]

It has been demonstrated in recent years that, by analogy with the theory of the non-adiabatic transitions in atom–molecule collisions, it is possible to devise a theory of the interactions of radiation with molecules.[208,209] This analogy is based on the concept of quasi-energy.[210] In the theory, which has so far been constructed for diatomic molecules, a wide variety of situations are observed, not all of which are encountered in atom–molecule collisions. This applies, for example, to the resonance Raman scattering, hot luminescence, and related phenomena, which can be treated from a single standpoint.[211]

The problems associated with non-adiabatic transitions are extremely varied. If one considers molecular collisions, then it is important to learn to calculate the probabilities of non-adiabatic transitions for multidimensional PES. Hitherto, theoretical studies have been restricted to cases where the PES depends only on one or at most two coordinates.[29] In certain cases more stringent requirements are imposed on the accuracy of the calculations of the PES, for example when the region of the quasi-intersection of the energy states is calculated. A fairly high accuracy is then essential for a reliable calculation of the probabilities of non-adiabatic transitions taking into account tunnelling.[29]

With the aid of the model of non-adiabatic transitions between quasi-energy surfaces, it is possible to formulate the important problem of the dynamics of electronically excited polyatomic molecules. For this purpose, it is necessary to extend the dynamic theory of non-resonance Raman scattering developed for diatomic molecules.[209,211] Further development of the theory of the interaction of a strong alternating field with molecules,[212] the dynamic theory of multiphoton processes in atoms and molecules,[213] etc. is also important. In particular, such a theory can indicate a way of determining the parameters of the non-adiabatic linkages in molecules from experimental scattering intensities and phase relations.

V. DEVELOPMENT OF THEORIES OF THE APPLICATION OF PHYSICAL RESEARCH METHODS TO CHEMISTRY

Theory has always played a significant role in the development of ways of applying physical methods to chemistry. It is sufficient to recall the Debye method for the determination of the electrical dipole moments or the theory of optical spectra without which molecular spectroscopy would simply not exist and which has in fact become the basis of the theory of molecular structure. Hundreds of such examples could be quoted. The corresponding theories have become an inseparable component of quantum chemistry. Among recent studies along these lines, mention should be made of the theoretical justification of the multipulse NMR method, which made it possible to resolve the fine structure of NMR spectra of solids and which has proved exceptionally important to chemistry,[214,215] the development of a theory for the investigation of the character of molecular motion in a condensed medium with the aid of a paramagnetic label,[216] and proof of the possibility of using the angular anisotropy of the Auger spectra for the investigation of the geometry of surface layers and adsorbed molecules.[217]

The appearance of a new physical method useful for chemistry frequently begins with the discovery of some kind of physical phenomenon which serves as the basis for a new research method after the appropriate theoretical interpretation. Theoreticians sometimes suggest how an existing method should be modified or amplified in order to apply it to chemical objects and to obtain a new type of information. Several theoretical problems whose solution may culminate with the creation of new experimental research methods in chemistry are quoted below as examples.

(1) Physicists have learned how to obtain beams of polarised electrons. The diffraction of such beams by the surface of a solid can undoubtedly yield unique information about the magnetic and spin states of the surface. However, it has so far been possible to obtain polarised beams only at very low temperatures and in an ultrahigh vacuum and the intensity of the beams has been low.[218] This very greatly restricts the scope of their application. The task for quantum chemists is, on the one hand, to find systems which polarise electrons under less severe conditions and ensure a sufficiently high intensity of the beams and, on the other hand, to develop a theory of the diffraction of polarised electrons in relation to chemical problems.

(2) It has been recently discovered that, when fast molecular ions pass through films, their electron clouds are "stripped off" and the molecule decomposes into charged fragments which fly apart under the influence of Coulombic forces ("Coulombic explosion").[219] The angular and energy distributions of these fragments can, generally speaking, reflect both the structure of the initial molecular ions and the properties of the film. It is extremely likely that the development of the appropriate theory will permit the creation of a new research method.

(3) The method for the indirect detection of electron magnetic resonance (IDMR), for example, detection with the aid of luminescence, made it possible, by virtue of its high sensitivity, to obtain much unique information about the intermediate species in chemical reactions, about the mechanism of the transfer of valence, etc.[220,221] It is promising and feasible to apply the IDMR method to the study of a process involving charge transfer between ions in the liquid phase. It is also of interest to examine the question of the specific features of the application of the IDMR method to the study of processes on the surface of a solid. It is natural to begin the solution of these problems with the development of appropriate theories.

(4) It is known that, under the conditions of a shock wave in the solid phase, many interesting effects are observed, for example, intense polarisation of the specimen, a change in the direction and rate of reactions, etc.[222,223] Apart from high pressure, a high temperature is characteristic of a shock wave. It would be very attractive to create a theoretical model of such processes and to show experimenters what experiments should be formulated in order to test the model and then to explain the observed effects at the molecular level and possibly to create a new method for the investigation of shock waves.

(5) Laser chemistry has so far taken only the first steps. It is known that the chemical action of the laser beam can involve not only the selective excitation of vibrations but also the excitation of the electron cloud.[224] For example, appropriate action by a laser entails the ready occurrence of the reaction[225]

$$Na + HgCl_2 \rightarrow NaCl + HgCl$$

The laser method for the separation of isotopes is based on the selective excitation of electrons. The task for quantum chemistry is to develop a detailed mechanism of the reactions of the laser-excited species and to recommend how experiments should be set up in order to achieve the catalytic action of the laser beam on chemical reactions.

VI. APPLIED PROBLEMS

1. Materials Science; Computer Search for New Compounds and Materials

As mentioned above, quantum chemistry has always served as the foundation which ensured the development of new ways of investigating matter and even the creation of whole branches of natural science, which ultimately has had enormous practical importance. It is sufficient to recall molecular spectroscopy mentioned above, which would be unable to solve many applied problems without the appropriate quantum-chemical theory. However, apart from such indirect influence on practice, quantum-chemical methods are resorted to with increasing frequency for the direct solution of specific applied problems, for example, the problems arising in materials science. One may quote a series of examples where quantum-chemical calculations proved useful in determining the relation between the macroscopic properties of materials and their atomic-molecular structure and ultimately in the solution of technological problems.

We may mention the calculations of diffusion coefficients in solid materials as one such example. These calculations are of special interest if the study of diffusion is hindered as a consequence of say, high radioactivity. Theoretical investigation of diffusion at the atomic-molecular level is also important in order to be able to understand the mechanics of the process and to create a basis for the treatment of more complex transport processes.[226] A model calculation of the activation energy for the diffusion of helium in nickel made it possible to understand the nature of the potential barrier and to elucidate the role of electronic relaxation and of the degree of involvement in the process of various electron layers of the nickel atom.[226,227]

Calculations of the physical characteristics of impurities and of their influence on the properties of materials are also important. For example, the geometrical and energy characteristics of the impurity centre, its influence on the intrinsic defects in the solid, etc. have been calculated by quantum-chemical methods. Such calculations for impurity carbon in iron helped to explain many effects important for engineering.[226]

Quantum-chemical methods have helped in the solution of certain problems of interest for the theory of solar cells, for example, the probabilities of the non-radiative decomposition of excitons in solid hydrogen fluoride have been calculated.[226]

An interesting quantum-chemical calculation has been performed to elucidate the mechanism of the oxidation (and inactivation) of a graphite moderator in a nuclear reactor. Calculations showed that the oxidation takes place at defects on the graphite surface and that the diffusion to these defects of molecules such as those of H_2O and CH_4 is much faster than the diffusion of oxygen. The addition of a small amount of, for example, methane to the coolant (CO_2) slows down the oxidation of graphite, because methane rapidly occupies its active centres.[226]

Quantum-chemical calculations have made an important contribution to the solution of the problem involving the search for the optimum accumulator (carrier) of hydrogen as a source of chemical (fuel) and nuclear energy.[228] Transition metal alloys are usually employed for this purpose. Calculations permitted the determination of the maximum possible store of hydrogen in the given alloy and showed, in particular, that amorphous bodies are capable of carrying more hydrogen than crystals of similar composition.

The development of the theory of the Jahn–Teller effect led to the prediction of a practically important phenomenon—giant magnetostriction.[201,229] The theory has been confirmed experimentally.[230]

One may point to a striking example where quantum chemistry played an important role in the solution of one of the fundamental problems in the physics of elementary particles—in the determination of the true mass of the neutrino at rest. Kaplan and co-workers[231,232] investigated the rearrangement of the electron clouds of a number of molecules of tritiated hydrocarbons and certain other compounds occurring on β-decomposition. The results of the calculations were used to interpret experiments designed to find the rest mass of the neutrino.[233] Analogous but more accurate calculations were subsequently performed by other workers.[234,235]

An increasing tendency to calculate by quantum-chemical methods the stability and properties of compounds which have not yet been synthesised, to make recommendations for the optimisation of the conditions and pathways leading to the synthesis of new medicinal preparations, etc. has been observed in recent years. For example, the stability of the C_{60} molecule, which, in view of its spherical shape has been called footballene, has been demonstrated theoretically.[236,237] Its stability was predicted as early as 1973 by the Hückel method.[238] Footballene has not yet been synthesised, but there are experimental data confirming its existence and high stability.[239,240] We may also note that quantum-chemical calculations have helped in the synthesis of a new effective antibiotic—quantamycin.[241] According to the recommendation arising from the quantum-chemical calculations, it has the composition and structure such that the negative qualities of its analogue (lincomycin) are eliminated.

The computer assisted search for new chemical compounds and materials with properties specified beforehand and the development of the optimum methods of their synthesis will undoubtedly be expanded still further in the immediate future Computer modelling will also be directed to the search for means of protecting materials against radiation,[242] the study of their behaviour under extreme conditions, and the solution of many other problems important for practical purposes.[243]

2. Quantum Molecular Biology

One of the most important fields in which quantum chemistry has been applied is molecular biology. During the last decade, considerable progress has been seen in this direction and has been represented increasingly at international congresses and conferences on quantum chemistry; conferences devoted specifically to this topic have also been organised. Analysis of the relevant questions is outside the

scope of our task. However, in order to demonstrate the specific features of this extensive field, we shall quote one example.

The striking selectivity of photochemical biosynthesis is known: under natural conditions, billions of tonnes of green matter are generated each spring in several weeks virtually without waste, while under laboratory conditions in analogous processes the yield of the required product reaches no more than 50%. The question arises what is the mechanism of this surprising single-channel nature of the process (purity of the biosynthesis), which is comparable to the selectivity of the action of enzymes. Quantum chemistry should help in the solution of this problem.

The specific features of molecular biology and the exceptional advances in gene engineering give grounds for the expectation that the use of biomaterials and biotechnology is more promising for the creation of the new generation of electronic computers[244] than that of the usual chemical compounds and methods.[245] Theoretical analysis of the possible versions of the structure of the constituent elements of a biocomputer is a task of current importance, to the solution of which modern quantum chemistry can make a definite contribution.

It must be emphasised that many major problems in molecular biology and pharmacology can be solved and are already being solved with the aid of computer modelling. These problems include, for example, the prediction of the biological activity of chemical compounds.[246,247] The simplest version of such predictions is as follows. The structures of a series of compounds, already known as active in the desired sense, are calculated quantum-chemically, the structural and electronic feature characteristic of the given activity are established, and new compounds having these features are then synthesised.

VII. DEVELOPMENT OF QUANTUM-CHEMICAL METHODS

As mentioned above, effective research methods have now been developed in various fields of quantum chemistry. Powerful procedures have been created in the theory of elementary processes in the gas phase, in the theory of magnetic, electronic, and vibrational relaxation of condensed phases, theoretical methods for reactions in solutions, theories of the interaction of matter with radiation, and many others have been greatly developed. Considerable efforts by theoreticians and mathematicians have been directed to the solution of the many-electron problem. Here studies have been prosecuted in two directions: (a) the improvement of semiempirical computational methods; (b) the development of effective non-empirical computational methods (calculations from first principles—*ab initio*). *Ab initio* methods have been developed mainly by expanding the initial basis set of one-electron functions in order to achieve the maximum possible approach to the Hartree–Fock limit and to develop effective methods for taking into account the correlation of electrons.[248]

At one time it appeared that non-empirical calculations should displace the semiempirical methods, because the former are more rigorous and in the limit yield accurate results. However the improvement of *ab initio* methods was very slow: on average (according to the data over a period of 20 years) the size of the systems in which it was possible to take into account correlation effects increased only by one and a half electrons per year.[249] The chemistry of large molecules therefore developed independently of these calculations. Furthermore, it was found that, as the non-methods are improved and the number of electrons in the system is increased, there is a catastrophic growth in the necessary computer time, which leads to a dramatic increase in the cost of calculations. When ultrafast computers (supercomputers) are used, the machine time is shortened, but the cost of the calculations does not fall but actually increases (approximately by a factor of 100) as a consequence of the increase in the cost of the work of the computer per unit time.[250]

Thus the view that *ab initio* calculations on molecules with a high degree of accuracy are not promising for the majority of chemical fields, since such calculations have to be confined in practice to comparatively small molecules, merits consideration. The problem of the development of sufficiently effective semiempirical methods, which would be comparatively cheap and "fast" and which would reproduce correctly the principal characteristics of molecular systems therefore comes to the fore. Certain promising approaches to the improvement of semiempirical computational methods have been published recently. For example, on the basis of the idea put forward by Burshtein and Isaev,[251] Dewar[250] proposed a new version of a semiempirical method, which is almost free of the most significant disadvantages of the previous versions.

It is possible to find in the literature a number of convincing examples where the semiempirical calculations, using the already existing methods, proved to be extremely useful and were found to have a predictive power (see, for example, Refs. 252–262), although, as is well known, not all the properties of molecules can be reproduced with equal adequacy by such calculations.

Together with this, there remains naturally the task of finding new methods for the solution of the many-electron problem. Such methods are essential in the first place for calculations on very large molecules, for which entirely satisfactory methods have not yet been created.[263] It may be that here one should abandon the standard procedure involving a simple extension of the models existing for small molecules and that an attempt should be made to find new modelling methods. The method of the density functional[264–267] merits attention. One cannot rule out the possibility that progress in computational quantum chemistry will be achieved using approaches in which wave functions do not appear at all.[263] Mention should also be made of a promising but more specific possibility of studies where new (sometimes quite unexpected) relations are established between different properties of molecules or physical quantities, without solving the Schrödinger equation, on the basis of general theorems such as the Hellmann–Feynman theorem or the hypervirial theorems.[268]

The following comment should also be made concerning non-empirical calculations and the prospect of obtaining with their aid highly accurate results. As the calculation becomes more accurate, there is a gradual abandonment of simple models. In the limit of the "accurate" calculation, the clarity of the results is completely lost; as in the case of an experiment, the latter must be re-interrupted anew, since otherwise the result of the calculation will be merely a "dead" numerical value. In other words, even after very extensive computerisation of quantum chemistry the physical model will not lose its heuristic role. The development of science during the last 10–20 years confirms this view. It is sufficient to recall, for instance, the role which orbital symmetry conservation rules[1] or the concept of frontier orbitals[2–4] have played and are playing in the development of chemistry. Such generalisations are perhaps more important for progress in science than hundreds of other laborious calculations.

The same may be said also about other ways of applying computers in quantum chemistry. The method of molecular

dynamics and the method of statistical sampling (the Monte Carlo method) can only supplement but not replace studies based on physical models. Clearly, there exist very complex processes which cannot be investigated by procedures other than those involving computer modelling.

It is known that the computer itself does not generate directly new physical or chemical ideas. It is a means for the completion of the development of a new idea or a new method and in this sense computers play a very important but subsidiary role in the development of science. At the same time, one should also bear in mind two factors. In systematic studies using a computer, the investigator acquires a new ("computer") form of thinking: a computer experiment suggests to him an effective way of solving the problem which is in essence associated with the computer. Thus, a kind of feedback is generated. The Luzanov method—the method for the operator reduction of the density matrix—may serve as an example of such a situation.[269] It is based on the idea of developing a mathematical apparatus for taking into account the correlation effects which could be readily translated into machine language. The specific features of computers suggested that an algebraic apparatus can serve for this purpose. With its aid, the author was able to develop a method which takes into account effectively configuration interaction without an explicit use of wave functions.

The second factor is associated with the fact that the computer is in essence an effective instrument for carrying out a kind of computer experiment. If one expects from such an experiment not a simple individual numerical value of some kind of parameter but a broader kind of information about the test system, then as in any experiment, the results have to be interpreted after the completion of the calculations. Such interpretation can lead to the appearance of new representations and new ideas important for the solution of the problem as a whole and in this way the computer can prove to be an indirect source of new ideas.

Fundamental ideas in quantum chemistry are known to have appeared before the invention of computers. Among them one may include the Heitler–London method (1927), the idea of molecular orbitals [Hückel, Mulliken (1930–1932)], the crystal field–ligand field theory [Boethe, Van Vleck (1929–1935)], the self-consistent field method [Fock (1930)], the Jahn–Teller theorem (1937), the transition state method [Eyring, Polanyi (1935)], the Kramers method in the theory of reactions (1940), and others. Unfortunately one should note that by no means all the major ideas were properly understood and adopted sufficiently rapidly. This happened with ligand field theory, whose principles are being introduced into chemistry only after 25 years had elapsed since the first publications; the Jahn–Teller theory appeared in the scientific literature for more than a quarter of a century as an elegant artifice without experimental confirmation and application; the Kramers method remained unknown to chemists for more than 30 years. As a result of the last factor, virtually no account was taken for a long time of dynamic effects, as mentioned above, in the theory of reactions in solutions. The task for theoreticians apparently consists, in particular, in helping the penetration of new ideas into practical experimental research.

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It follows from the foregoing that quantum chemistry has been playing an increasingly important role in the development of chemistry as a whole and has been making increasing contributions to practical research and to new technology. This mission of quantum chemistry is being achieved in conjunction with experiment. The task is to strengthen comprehensively such linkages with experiment, to strengthen the influence of theory on experimental research, and to seek new ways of applying physical research methods in chemistry. At the same time it is necessary to improve quantum-chemical methods and to develop effective and cheap methods for calculations on molecular systems. It is to be expected that the general trends in the development of quantum chemistry in the coming years will involve the theory of chemical reactions, theoretical materials science, and molecular biology. The advances in the development of these theories during the coming decades may prove comparable to the advances in the theory of molecular structure during the last 20–30 years.

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Layered Silicates as Catalysts

M.I.Rozengart, G.M.V'yunova, and G.V.Isagulyants

The structure of layered silicates, mainly smectites, and the synthesis of similar minerals, including fixed clays with pores exceeding in size the inlet apertures in zeolites are examined. Such clays are capable of catalysing the reactions of even large molecules, having a kinetic diameter in excess of 1.0 nm, which cannot penetrate into zeolite cavities for steric reasons. Certain reactions occuring in the presence of layered and fixed clay minerals are considered.
The bibliography includes 184 references.

CONTENTS

I. Introduction 115
II. The structure of layered silicates 115
III. The synthesis of layered silicates 117
IV. Certain physicochemical properties 119
V. The nature of the active surface 120
VI. Catalysis in the presence of layered silicates 121

I. INTRODUCTION

Clays, which form part of the group of natural layered aluminosilicates, have long been used for the purification and clarification of petroleum fractions by virtue of their adsorption properties. Much later clays came to be used as catalysts of organic reactions.

The advances in catalysis in the presence of amorphous aluminosilicates[1] and then synthetic crystalline aluminosilicates (zeolites)[2-6] diverted attention from the application of clays as catalysts and greatly weakened the interest in research on these lines. However, during the last decade, numerous studies have again been published on the application of layered silicates as catalysts of organic reactions.[7-11] This was promoted by the brilliant successes in the synthesis of minerals, including clay minerals, and the appearance of new refined methods for the determination of their structure and properties. A new class of catalysts, which are called "pillared sheet silicates" and also cross-linked or fixed layered silicates, were created in the 1970s. There is virtually no information about them in the Soviet literature. The appearance of fixed layered silicates, including clays, coincided with the time when interest was aroused in compounds resulting from intercalation in layered substances such as graphite,[8-12] clays,[7-11] phosphates, and certain other compounds of quadrivalent metals.[8]

Layered silicates, including clays, constitute three-quarters of the sedimentary rocks in the Earth's crust.[13] Their deposits have been created as a result of the weathering of hyperbarites, basalts, granites, and especially volcanic ash, glasses, tuffs, and different types of pumice. The principal chemical components of layered silicates are SiO_2 (30–70%), Al_2O_3 (10–40%), and H_2O (5–10%). Among the clay minerals constituting the basis of clays, which have found applications as adsorbents and catalysts, mention should be made of the kaolinite $[Al_4](Si_4O_{10})(OH)_8$.[9,10] Various smectites, capable of swelling, including the dioctahedral smectites[9,10] (see Fig. 2 below), montmorillonite $M^{n+}_{x/n}[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4$ and beidellite $M^{n+}_{x/n}[Al_4](Si_{8-x}Al_x)O_{20}(OH)_4$, and the trioctahedral smectites hectorite $M^{n+}_{x/n}[Mg_{6-x}Li_x](Si_8)O_{20}(OH, F)_4$ and saponite $M^{n+}_{x/n}[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$ are of greatest interest. Vermiculites, which swell with much more difficulty, as well as the micas muscovite $K_2[Al_4](Si_6Al_2)O_{20}(OH)_4$ and phlogopite $K_2[Mg_6](Si_6Al_2)O_{20}(OH)_4$, where M are exchangeable cations are also layered silicates; the cations forming part of the composition of the octahedral layer are enclosed in square brackets (see Section II) and the cations forming part of the composition of the tetrahedral layer are indicated in round brackets (again see Section II). In reality, the composition of real clay minerals may differ from the idealised formulae quoted above. Furthermore, clays usually contain different admixtures: carbonate, gypsum, iron oxides, etc. as well as plant or animal residues. All the most important properties of clays and clay minerals depend mainly on the chemical and mineral composition and the proportions of different grain sizes.

Pure montmorillonite clays (bentonites), industrial deposits of which exist in various regions of the USSR, have acquired the greatest practical importance as sorbents and catalysts. Mainly montmorillonites and hectorites, both natural and synthetic, constitute the basis of a new type of fixed layered aluminosilicate catalysts.

II. THE STRUCTURE OF LAYERED SILICATES

The majority of layered silicates are made up mainly of two structural fragments:[16-19] a network of silicon–oxygen tetrahedra SiO_4 (the *T*-network) and the network of aluminium-oxygen octahedra $Al(O, OH)_6$ (the *O*-network). In the ideal model, it is assumed that the sizes of the tetrahedra and octahedra are comparable, the Si^{4+} ions being located in the centres of the tetrahedra whose vertices are occupied by oxygen ions. Each O^{2-} ion, lying in the basal plane (the plane comprising oxygen triads lying at the bases of the tetrahedra) of the *T*-network, made up in accordance with the hexagonal motif, joins together two tetrahedra (Figs. 1*a*, 1*b*, and 1*c*). The octahedra, in the centres of which aluminium or magnesium ions are located, sometimes substituted by the ions of other elements, have edges in common, on which there are two common oxygen ions, and form the *O*-network, also in accordance with a hexagonal motif (Fig. 1*d*). Depending on the valence of the cations and on the degree of occupation of the *O*-positions by them, dioctahedral networks arise (Fig. 2). The octahedra in the dioctahedral networks are populated mainly by tervalent cations (Al^{3+}, Fe^{3+}), pairs of such octahedra meeting at a common lateral edge; trioctahedral networks include predominantly bivalent cations and three octahedra meet at a common lateral edge in each case.

The Si^{4+} cations in the *T*-network can be isomorphously substituted by Al^{3+}, Fe^{3+}, etc. ions, while the Al^{3+} ions in the *O*-network can be similarly substituted by Mg^{2+}, Fe^{2+}, Li^{+}, etc. ions. The substitution of a cation by an ion with a lower valence leads to the appearance of one negative charge in the layer, which creates conditions for the manifestation of acid properties by the clays. In those cases where charge-compensated substitution takes place, for example, the substitution of $2Al^{3+}$ by $3Mg^{2+}$, the charge of the layer does not change [see Barrer[7] (p.538) and also Osipov[18]].

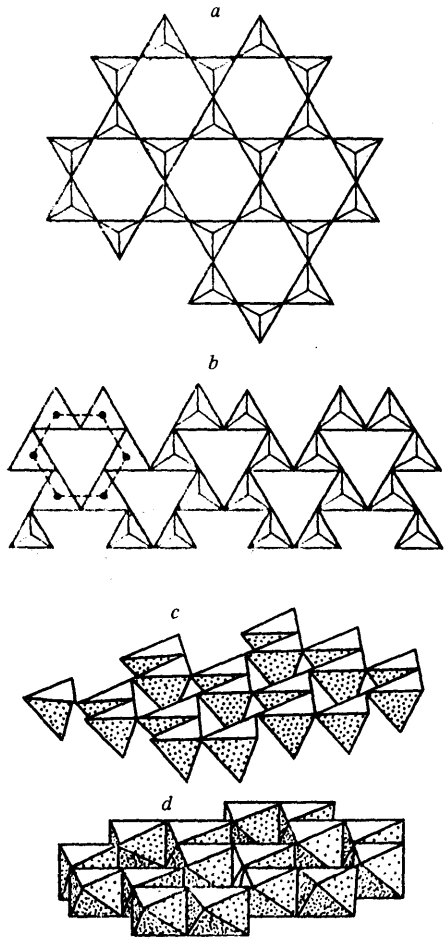


Figure 1. Models of the principal structural fragments of layered silicates:[7,8,17] *a*) and *b*) tetrahedral silicon–oxygen networks (*T*-network) (in the hexagonal motif in Fig.1*b*, the dots indicate the apical oxygen atoms of the tetrahedra and the dashed lines designate their hexagonal disposition); *c*) *T*-network in the axonometric representation; *d*) octahedral network (*O*-network) in the axonometric representation.

The *T*- and *O*-networks are joined together via the O^{2-} ions, forming layers made up of two, three, and more networks (Figs.3 and 4) constituting the basis of various clay minerals. All the vertices of the tetrahedra in each *T*-network are rotated towards the *O*-network. Kaolinite, for example, belongs to structures made up of two-network layers (1:1) and containing one *T*-network and one *O*-network in each case. Smectites (montmorillonites, hectorites, and hydromicas), vermiculites, as well as micas have a structure in which two *T*-networks are joined to an *O*-network between them (2:1, *TOT*-minerals). The distance *d* from the *T*-network of one layer to the *T*-network of an adjoining layer arranged in the same way and the size Δd of the gap between the layers are characteristic parameters of layered silicates (Figs.3 and 4).

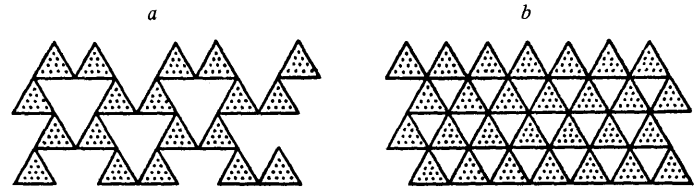


Figure 2. Types of octahedral networks:[16,17] *a*) dioctahedral; *b*) trioctahedral (only the upper faces of the octahedra are represented).

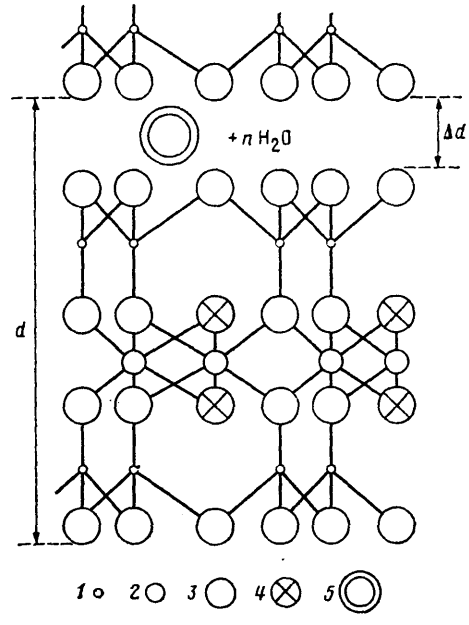


Figure 3. Schematic representation of the structure of montmorillonite:[7,8] 1) Si; 2) Al; 3) O; 4) OH; 5) intercalated cations.

In real clay minerals, the bases of the tetrahedra are not located in one plane, the cations being displaced relative to the tetrahedra and the pattern of the *T*-network differing from the ideal hexagonal motif. The octahedra are frequently flattened in the direction at right angles to the

planes of the networks. A twist in the arrangement of the octahedra in the dioctahedral network in the plane coplanar with the basal plane has been noted, which also distorts the planar surface and its hexagonal motif.[16] This influences strongly the structure of layered silicates: the dimensions of the tetrahedra and octahedra cease to be comparable, the surfaces of the octahedra become non-coplanar, and the basal surfaces of the layers acquire an irregular wavy structure.

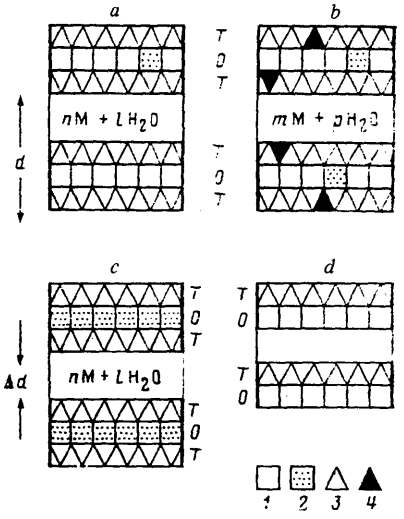


Figure 4. Schematic representation of the structures of certain layered silicates according to Frank-Kamenetskii et al:[16] *a*) montmorillonite; *b*) hectorite; *c*) vermiculite; *d*) kaolinite; 1) aluminium–oxygen octahedron; 2) magnesium–oxygen octahedron; 3) silicon–oxygen tetrahedron; 4) aluminium–oxygen tetrahedron; M = intercalated cations.

In the layered silicates having the *TOT*-structure, the gap between the layers is made up of the isotypical surfaces of the *T*-networks, which are held by the dispersion forces of the silicon–oxygen tetrahedra and by the electrostatic forces arising between the negative charges of the opposite layers and the cations (mostly Na^+ and Ca^{2+}) located between them. Depending on their size, the cations are fully or partly "pressed" into the free space between the tetrahedra, generating an additional force drawing the layers together. In terms of this capacity, the ions can be arranged in the series Li < Na < K < Mg < Pb < NH_4 < Co < Al[19] (p.179). However, this sequence frequently breaks down. Thus if the sizes of the cation and of the apertures of the *T*-network are similar, then such a cation is held more strongly.

The space between the layers in many layered minerals having the *TOT*-structure, such as smectites, vermiculites, etc. contains a certain number of water molecules involved in the formation of the mineral. These molecules prevent the collapse (complete adhesion) of the layers. The layered and two-dimensional primary porous structure arises in this way (it is denoted in the literature by 2*D* or 2*d* in contrast to the three-dimensional 3*D* or 3*d* porous structure of zeolites).

Cations are also located on the lateral surfaces of the crystals. Like the interlayer cations, these can be readily exchanged for a wide variety of inorganic and organic cations. Furthermore, as a result of the abrupt termination of the *T*- and *O*-networks, valence-unsaturated atoms capable of adsorbing ions and molecules are formed on the lateral surface. It has been suggested that up to 80% of the exchangeable cations are present in the interlayer space and up to 20% on the lateral surface[7] (p.537).

The crystals of clay minerals are joined together into small scale-like, ribbon-like, or tubular particles sometimes of colloidal size, which tend to aggregate and generate a secondary porous structure between the particles.[8,20,21] Table 1 presents data on the shapes and dimensions of the particles of certain clay minerals.

Table 1. The shapes and dimensions of the particles of certain layered silicates.[7,9]

Mineral	Shape of particles	Particle size, μm
Kaolinite	Hexagonal plates, frequently well formed, sometimes elongated	Width 100–4000; thickness 50–2000
Montmorillonite	Poorly differentiated shapes, rarely hexagonal, characteristic tendency towards formation of aggregates of particles	Diameter up to 1000 and above; thickness 1–20
Hectorite	Thin elongated plates	Length up to 3000; width ~100; thickness 1–2 and above

The occurrence of reactions between organic substances in the interlayer space in smectites at high temperatures (in excess of 200 °C) is prevented by the dehydration of the clays and the collapse of the layers induced by this. The temperature-dependent limitations imposed by the collapse can be overcome by introducing into the interlayer space thermally stable bulky cations which act as a kind of pillar and fix the layers at a specific distance preventing them from adhering closely after the removal of water or a solvent. This way of fixing the layers made it possible to create a new class of aluminosilicate catalyst—pillared sheet silicates.

III. THE SYNTHESIS OF LAYERED SILICATES

Clay minerals of constant composition, contaminated to a minimal extent by extraneous impurities (which is especially important for the development of catalytic systems), can be obtained synthetically. Layered silicates are synthesised under hydrothermal conditions (100–400 °C) or by fusing together mixtures of the initial oxides at 800–1500 °C.

The results of studies on the hydrothermal preparation of kaolin, montmorillonite, pyrophyllite, and other clay minerals at an increased pressure have been summarised in a review.[22] The conditions in the formation of montmorillonite have been examined and its properties described.[23] Montmorillonite is formed in alkaline media and the results of the synthesis are appreciably influenced by magnesium (in contrast to other cations).

It has been established that the dioctahedral montmorillonite is formed with a relatively small MgO content in the mixture of the initial oxides. With increase in the MgO content

in the mixture, a small admixture of a trioctahedral smectite is formed initially and this is followed by the appearance of large amounts of the latter. In order to obtain a well crystallised product, the hydrothermal treatment is carried out for several (6–7) days.[31] A decrease in the duration of the hydrothermal treatment entails a proportionate decrease in the exchange capacity of the mineral.[31] The influence of temperature and pressure on the formation of montmorillonite in the SiO_2–Al_2O_3–H_2O[29] and SiO_2–Al_2O_3–MgO–H_2O [30] systems has been studied in detail and the regions corresponding to the formation of montmorillonite and other minerals have been described with the aid of phase diagrams.[30] Depending on the pH of the mixture, it is possible to obtain a clay mineral with the *TO*- or *TOT*-structure. Thus the addition of HCl to the initial mixture leads to the formation of kaolinite, while the addition of NaOH induces the formation of montmorillonite.[32]

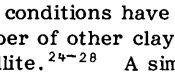
Hydrothermal conditions have also been used in the synthesis of a number of other clay minerals, for example, kaolinite and beidellite.[24–28] A simple method of synthesis of various clay minerals from a mixture of natural sand (or artificially precipitated SiO_2) and aluminium hydroxide (or $AlCl_2$) has been described.[32] The methods of synthesis of the so called "fluorotetrasilicate micas", in which some or all the hydroxy-groups have been replaced by fluorine atoms, have been developed vigorously in recent years,[33–36] especially by Japanese investigators. The fluorotetrasilicate micas constitute the basis of catalysts of a new type with a high thermal stability. The fluorohectorites obtained after the replacement of OH groups by fluorine are stable up to 800 °C [7] (p. 469). The OH groups can be replaced by fluorine atoms also in the hydrothermal treatment of a freshly prepared smectite with a solution of NH_4F or other water-soluble fluorine compounds.

Much attention has been devoted to the synthesis and study of the catalytic properties of the so called mica-montmorillonite,[37–40] which consists of a multilayered mineral with a random packing of mica and montmorillonite layers and an overall mica content ranging from 1/6 to 5/6. This mineral is frequently synthesised in such a way that it contains transition metal ions,[41–43] mainly nickel ions,[41,42] in the octahedral network. The composition of the product obtained by Heinerman's method[41] corresponds to the chemical formula $(Al_{1.08}Ni_{4.38})(Si_{6.62}Al_{1.38})O_{20}(OH)_{3.24}F_{0.76}(NH_4)_{1.38}$. As mentioned above, to prevent the layers from sticking together on raising the temperature, they are fixed at an appropriate distance.

The fixation of clays was first proposed more than 30 years ago.[44] In order to attain a constant porosity in clays, tetraalkylammonium ions have been used. However, the prospects for the employment of clay minerals in order to develop catalysts of a new type arose only when the fixation was achieved with the aid of inorganic compounds, namely the oligomeric aluminium and zirconium and then bismuth, chromium, etc. hydroxo-cations (Table 2). The insertion of an oligocation in clay minerals takes place fairly readily as a result of exchange with the interlayer cations. At the same time, in the presence of an excess of Al_{13} oligocations, the amount of bound aluminium calculated per unit cell varies within narrow limits (2.78–3.07), is not correlated with the charge determining the exchange capacity of the clay, and is independent of the charge distribution among the layers, which is extremely non-uniform in smectites and can vary from layer to layer by a factor of two.[60,61] This led to the hypothesis[62] that the adsorption of the oligocation entails the formation of a more or less uniform monolayer of polyoxo-cations on the surface of the clay. In this case the distance between the pillars is determined by the radius of the hydrated cations, which can in fact account for the uniform distribution of the pillars in the interlayer space after the dehydration of the fixed smectite.

The introduction of aluminium and zirconium oligocations leads to the formation of thermally stable clays exhibiting molecular-sieve and catalytic properties and having a specific surface of 200–500 $m^2\ g^{-1}$ and an interlayer gap Δd in excess of 0.9 nm.[49,50,63–68]

Table 2. Compounds used for the fixation of clays.

Name	Formula	θ, °C *	Refs.
Tetraalkylammonium	Alk_4NH	<250	[7, 44]
Bicyclic amines		<250	[45, 46]
Fe(II) and Cu(II) metal chelate complexes	$[Fe(2,2'\text{-bipyridyl})_3]^{2+}$; $[Cu(1,1'\text{-phenanthroline})_3]^{2+}$	<450	[47, 48]
Al oligocations	$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$; $[Al_{26}O_8(OH)_{52}(H_2O)_{20}]^{10+}$	>500	[49]
Zr oligocation	$[Zr_4(ON)_{12}(H_2O)_{12}]^{4+}$	~800	[50–52]
Bi oligocation	$[Bi_6(OH)_{12}$	>500	[13]
Cr oligocation	—	>500	[53, 54]
SiO_2 polymers	—	>600	[55–58]
Nb and Ta complexes	$[M_6Cl_{12}]^{2-}$	>600	[59]

* Thermal stability of fixed clays (natural clay is stable up to ~200 °C[7]).

As can be seen from Table 2, fixation increases the upper limit to the thermal stability from 200° to 550–800 °C. The fixation of clay minerals by oligomeric hydroxo-cations makes it possible to obtain aluminosilicates with a regular structure, the size of the cavities in which is significantly greater than in coarsely porous zeolites, including faujasites. This led to the possibility of using fixed clays for the catalytic reactions of large molecules, to which the internal surface of zeolites is inaccessible.

The aluminium oligocation (known in the U.S. industry as "chlorohydrol") is used most widely as a fixing agent and has been more thoroughly investigated than other such agents. It can be obtained by various methods: by dissolving metallic aluminium in a boiling solution of $AlCl_3$ [69] or in an NH_4Cl solution[70] and by hydrolysing $AlCl_3$ dissolved in water with sodium carbonate (either solid or in solution) at 90–100 °C.[71] The use of different aluminium salts yields similar results.[62] It has been suggested that the principal species in the aluminium oligocation is the so-called Keggin cation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$,[69,72] consisting of a central tetracoordinate Al^{3+} ion surrounded by twelve AlO_4 octahedra joined via the common edges.

In order to increase the molecular weight of the oligocation, chlorohydrol is subjected to ageing by boiling the solution for 1–48 h or by treating it with ammonia, alkali, and metallic magnesium.[66] The Al_{13} oligocation then dimerises with formation of the cation $[Al_{26}O_8(OH)_{52}(H_2O)_{20}]^{10+}$.[66]

The zirconium oligocation is obtained by hydrolysing zirconyl chloride $ZrOCl_2.8H_2O$ in sodium carbonate solution. After the solution has been aged for 24 h, an oligomer having a molecular weight of ~1000 is obtained.[66] The method of fixation of clays described by Vaughan et al.[66] has been used virtually without change in many investigations.

The high thermal stability of the smectites fixed by the Al_{13} and especially Zr_4 oligocations is attributed to the formation of metal oxide clusters as a result of the dehydroxylation of the hydroxo-cations at an elevated temperature. In the case of the Al_{13}-montmorillonite, this reaction proceeds in accordance with the mechanism[73]

$$[Al_{13}O_4(OH)_m \cdot p\,H_2O]^{n+} \rightarrow 6.5\,Al_2O_3 \cdot q\,H_2O + n\,H^+$$

However, there is no information about the structure of the cluster (the so called pillar) or about the disposition of the protons in the oxide compound.

Chromium is also included among the metals capable of forming oligocations.[53,54] The transparent solution of the chromium oligocations obtained from chromium nitrate and ammonium hydroxide is violet in colour. The bentonite fixed by such cations has a specific surface of 165 $m^2\ g^{-1}$ and a micropore volume of 0.03 $cm^3\ g^{-1}$ and d amounts to 1.2–1.4 nm (0.96 nm in the initial clay).

There have been reports[74–76] of the synthesis of Fe-fixed smectites prepared using the trinuclear hydroxoacetatoiron(III) nitrate complex $[Fe_3(OAc)_7(OH)_2(H_2O)].NO_3$. After the clay has been heated, the complex cations, introduced by ion exchange, are converted into oxides, which serve as the pillars; the value of d established is 1.66 nm.

Although fixation with the aid of polynuclear hydroxo-cations makes it possible to obtain stable clays with a large free space between the layers, the number of elements capable of forming the oligomers is limited. Ways of extending the number of fixing agents are therefore being sought. For example, the silicic acid obtained by the hydrolysis of silicon acetylacetonate cations in the interlayer gap[56,57] or of polychlorosilanes[58] can be introduced into montmorillonite. In such cases the clay is usually allowed to swell beforehand in an organic solvent (amine or alcohol). After heat treatment, the inserted SiO_2 is capable of maintaining the layers at a distance of 1.26 nm from one another; the specific surface of the clay fixed by silica and measured with respect to nitrogen is 240 $m^2\ g^{-1}$.

It has been suggested that aluminium and zirconium as well as aluminium and silicon copolymers be used for fixation.[66] The properties of catalysts prepared on the basis of clay minerals cannot be improved by the fixation of the latter. Thus a decrease in the activity of the catalyst was noted[77] when a copolymer of aluminium and silicon was used as the fixing agent. The hydrolysis and oxidation of the cations $Nb_6Cl_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ make it possible to obtain fixed clays with an interlayer gap $\Delta d > 1.0$ nm. These clays are stable up to 400 °C.[59]

Whereas the fixation of clay minerals determines their primary interlayer porosity, the secondary porosity between the clay particles depends greatly on the conditions in the drying of the fixed mineral.[62] Thus drying in air gives rise to a product in which the size of the external secondary pores is 0.6–0.9 nm, while the mineral dried by subliming water from the specimen frozen beforehand is capable of adsorbing molecules with a kinetic diameter† greater than 1.0 nm. It has been suggested that drying in air entails close layer-by-layer adhesion of the mineral particles and the volume of secondary pores becomes small. Drying by sublimation promotes a disordered agglomeration of the particles, which gives rise to a larger free pore volume between them.

†The kinetic diameter[62] or the critical diameter[7] (p. 293) is the diameter of the van der Waals section through the molecule.

IV. CERTAIN PHYSICOCHEMICAL PROPERTIES

The most characteristic and important property of clay minerals, especially montmorillonites and to a lesser extent hectorites and vermiculites, is their ability to swell both in water and water vapour as well as in certain polar organic liquids. The molecules of the substances inducing the swelling are inserted into the interlayer space and move the layers apart. For example, when one, two, or three layers of water molecules are inserted in montmorillonite, d increases from 0.95 to 1.24, 1.54, and 1.9 nm respectively. The montmorillonite in which the intercalated cations have been exchanged for Sr^{2+} can give rise to several intercalation compounds with butyrolactone (single-layer, two-layer, and three-layer), for which d is 1.3, 1.8, and 2.3 nm respectively.[19]

Some workers believe that paraffinic hydrocarbons are not sorbed by smectites containing small intercalated cations[7] (p. 434). According to other data,[15] intercalation does occur, but extremely slowly, and traces of moisture are essential for this purpose. Apparently, the presence of intercalated water leads to the delocalisation of alkali metal cations and intensifies their polar effect on hydrocarbons. The nature of the intercalated cation, which is important for the adsorption of polar compounds, does not influence appreciably the intercalation of n-alkanes.[78] Evidently the adsorption of saturated hydrocarbons is not due to ion exchange; their insertion in the space between the layers in smectites can be accounted for from the standpoint of the interactions of the molecular dipoles, induced by the mineral ions, with the surfaces of the clays.[15,78,79] There are data showing that the Ca- and NH_4-montmorillonites do not sorb n-hexane.[79] However, montmorillonite with intercalated $CH_3NH_3^+$, $(CH_3)_4N^+$, and $(C_2H_5)_4N^+$ ions sorbs saturated hydrocarbons, while montmorillonite containing a quaternary ammonium base with a long chain, for example, the didodecyldimethylammonium ion, adsorbs selectively paraffinic and aromatic hydrocarbons, and is used in gas–liquid chromatography.[7]

The intercalation of C_6–C_{10} paraffins in fixed clays takes place fairly readily,[81] is independent of temperature and the number of carbon atoms in the molecule, and leads to the filling of 50–60% of the pore volume. The heats of sorption in such clays are much lower than in zeolites and the rate of diffusion of the sorbates is several times higher.

The study of the adsorption of hex-1-ene on the Cr^{3+}-exchange montmorillonite by IR spectroscopy[82] shows that the alkene is protonated in this instance and that the 2-carbonium ion formed is linked to the primary coordination sphere of the intercalated cation. One of the hydrogen atoms in the water molecules in this primary sphere is involved in the formation of strong hydrogen bonds with the silicate layers, while others do not form such bonds and are directed into the interlayer space. These hydrogen atoms are in fact labile and protonate the alkene molecule.

Benzene and its substituted derivatives as well as tetralin and naphthalene are fairly readily intercalated in certain smectites, forming even a double layer.[78,83] The interaction of benzene with Cu^{2+}-montmorillonite results in the formation of coloured complexes:[84,85] in the green complex, benzene retains its aromatic character, while in the red complex its aromaticity is infringed, since the π-electrons become localised.[84,85]

Non-aromatic non-polar molecules are intercalated very slightly or not at all in layered silicates containing intercalated cations of small diameter, for example, Na^+ and Ca^{2+}. On the other hand, in the presence of large cations, for

example, the Cs^+ ion, intercalation takes place to an appreciable extent[7] (p.436). Another smectite, Ca-montmorillonite, swells effectively in saturated alcohols and glycols, which are capable of displacing water from the interlayer space, including water hydrating the cations. When a single layer of C_4–C_{18} alcohol molecules is intercalated in the smectite, the hydrocarbon group is arranged parallel to the basal plane (Fig. 5a). The hydrogen of the hydroxy-group is linked to the oxygen of the *T*-network via a hydrogen bond. On the other hand, if many molecules are intercalated, they are arranged almost at right angles to the basal plane (Fig. 5b) and the hydrogen atoms of not only the hydroxy-group but also of the methyl group at the opposite end of the chain form a hydrogen bond with the oxygen of the second *T*-network. With increase in the length of the hydrocarbon chain of the alcohol, the distance between the layers therefore increases. The layers move apart to an even greater extent after the intercalation of aliphatic acids.

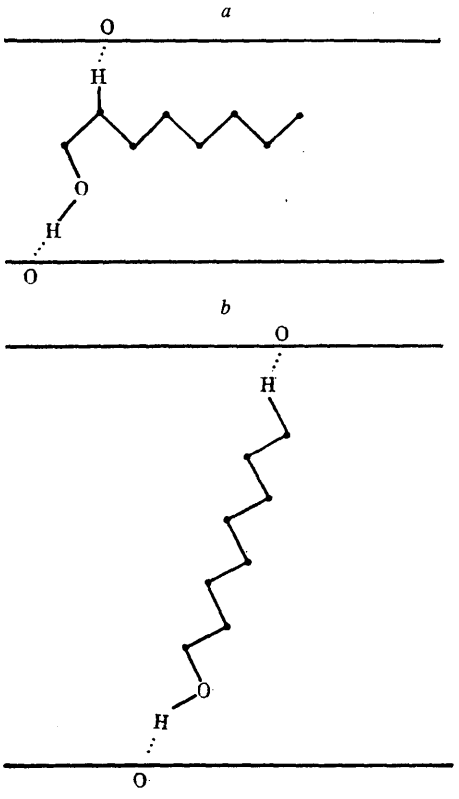


Figure 5. Models of the arrangement of n-alcohols in the interlayer space:[86] *a*) for the single-layer intercalation of the alcohol; *b*) for the maximum intercalation.

The removal of water and of intercalated organic substances, for example, on heating unfixed layered silicates, leads to a marked decrease in the interlayer space (the layers adjoin one another closely), which hinders the subsequent intercalation of substances and sometimes completely rules it out. On the other hand, if the inorganic intercalated cations have been exchanged for the ions of quaternary ammonium bases, then, after the removal of the intercalated substances, for example, water or alcohols, the distance *d* remains the same as before swelling[7] (p.461): the bulky ions prevent the layers from sticking together.

The ability of the intercalated cations to exchange, which was already mentioned in Section III, is important for the chemistry of layered silicates. The cation exchange takes place mostly in aqueous salt solutions, which can be achieved also in non-aqueous solutions, for example, alcoholic solutions. With increase in temperature, the rate of exchange also rises, but the exchange capacity diminishes, since some of the compensating cations move deeper into the network.[21] The exchange capacity diminishes particularly markedly when the specimen is heated above 300–400 °C; after such heating, the exchange capacity of clays is not as a rule restored, since the mineral is partly decomposed.

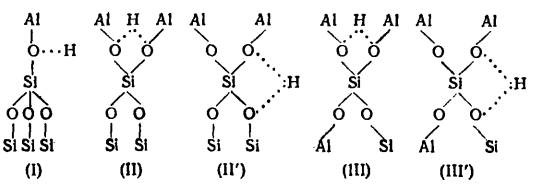
V. THE NATURE OF THE ACTIVE SURFACE

It follows from the data described in Section II that the active surface of layered silicates is extremely inhomogeneous. It is based on the basal surface of the *T*-networks with the lower valence cations built into these and the *O*-networks, which generates negative charges in the layer, the latter being neutralised by the intercalated cations. These *T*-networks bound both the crystal as a whole (part of the external surface) and the individual layers of the *TOT*-structure (internal surface). Another part of the external surface is made up of the lateral surface of the layers made up of the valence-unsaturated atoms of the *T*- and *O*-networks. Although the lateral surface of the cleaved layers does not exceed 20% of the total specific surface of the layered silicate (see Section II), nevertheless it has an appreciable influence on the character of the adsorption and of the catalytic action of the layered silicates.

It is known that the surface of a pure silicon–oxygen compound, for example quartz or ignited silica gel, is neutral. (Freshly prepared silica gel, heat-treated at a temperature not exceeding 500 °C, exhibits a weak acidity and catalyses the reactions of hexatrienes via an acid mechanism[87,88]). On isomorphous substitution of an Si^{4+} ion by Al^{3+}, the resulting aluminosilicate acquires acid properties, the nature of which is the same for all aluminosilicates, including zeolites; it has been most thoroughly investigated for the latter.

The aluminium atom inserted into a hydroxylated silicon–oxygen surface draws the electrons in the Al–O–Si–O–H group towards itself in an effort to fill its unoccupied *p* orbital, which polarises the –O–H bond[4] and, in the interaction with a water molecule, leads to the formation of an additional proton centre.

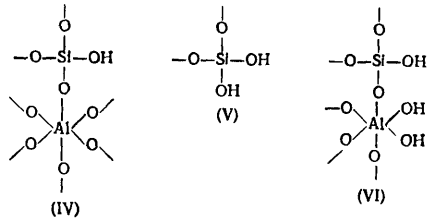
On the basis of quantum-chemical calculations for cluster models and the study of the IR spectra of aluminosilicates, it has been suggested[89,90] that there are several types of acid centres in both amorphous and crystalline aluminosilicates:



The highly acid centres are linked to the terminal siloxane OH group. The acidity of the bridging OH groups in centres of type (I) and especially (II) and (III) is somewhat reduced. The acid centres of types (II) and (III) can exist in the isomeric forms (II) and (II') and (III) and (III').

It is to be expected that acid centres are also present in layered silicates. The distance between them in such silicates usually exceeds the size of the aluminium ion and even the radius of action of the valence bonds.

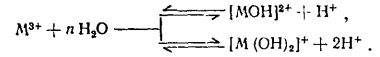
Valence-unsaturated atoms, giving rise to single (IV) and paired (V) and (VI) Brønsted acid centres differing in strength, appear on the lateral surface of the layers, especially when the crystal is cleaved:



(IV) (V) (VI)

The hydroxy-groups in (VI) can become capable of either cation exchange or anion exchange depending on the pH of the medium[9] (p.25). Furthermore, there are Lewis acid centres in montmorillonite both on the lateral surface of the crystal and on the basal surfaces.

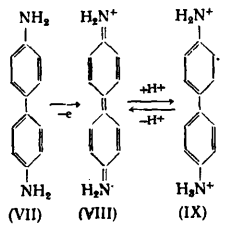
Acid centres arise in layered silicates also as a result of the interaction of water with intercalated cations, especially tervalent cations:



The degree of dissociation increases with increase in the polarising power of the cation in the sequence K < Na < Mg < Al.[93,94] In the presence of a large amount of water, the polarisation effect, arising when water is acted upon by the cation, weakens, since the influence of the cation is dissipated among a larger number of molecules and the pH of the medium approaches the values characteristic of the ion in solution. However, the concept of such a major role of exchange cations in generating the acidity of layered silicates has been questioned[18] (p.33). The hydroxy-groups of minerals can also serve as centres for the adsorption of polar organic compounds. Brønsted acidity predominates on clays containing 0.5–1.0% of water. For a lower level of hydration, the strength of the acid centres increases and the clay behaves more like a Lewis acid.[95,96]

The study of the interaction of clays with various amines led to the elucidation of the nature of the catalytic activity of layered silicates. Acid–base and oxidation-reduction reactions, leading to the formation of coloured radical-cations, take place when certain amines are adsorbed on clays.[97] The acid–base mechanism is especially characteristic of acid-washed clays. These clays act as proton donors, because their activity is greatly suppressed by treatment with bases, for example, ammonia. Oxidation-reduction reactions are relatively insensitive to treatment with acids and bases, but they are appreciably influenced by the presence of reducing agents such as $SnCl_2$.

The study of different types of treatment showed that colour reactions of clays with aromatic amines proceed with participation of Lewis and Brønsted acid centres. The reaction of benzidine with layered silicates has been most thoroughly investigated:[86,92]

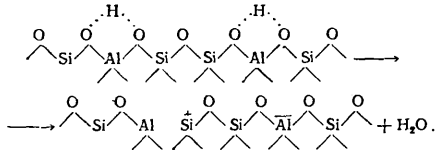


(VII) (VIII) (IX)

The proposed reaction mechanism involves electron transfer from the initial diamine (VII) (i.e. its oxidation) to the mineral with formation of the blue radical-cation (VIII) (a semiquinone). The stability of the colour can be explained by the conjugation of the unpaired $2p_z$ electron of the nitrogen atom with the π-electron system of the aromatic ring enhanced by the resonance of both rings. The blue colour is observed only at pH 2.5–6. At pH < 2, the proton adds to the unshared electron pair of the nitrogen atom in the radical-cation, giving rise to the yellow radical-dication (IX).

The adsorption of sodium polyphosphate or reductive treatment of the clay inhibits the colour reaction only partially. Its complete inhibition occurs only when both these factors act simultaneously. The hypothesis was put forward on this basis[86,92] that the diamine is oxidised on the valence-unsaturated aluminium atoms on the lateral surface, the process being inhibited specifically by polyphosphates, and on Fe^{3+} ions located in the octahedral network which react with the diamine in the interlayer gap via the *T*-network.

The similarity of the chemical nature of layered silicates and other aluminosilicates suggests that they all contain isotypical active centres and not only acid active centres. Thus strong electron-accepting centres, formed by the triply charged Si^{3+} and Al^{3+} ions of the defect structures, as shown below in the two-dimensional scheme for zeolites and aluminosilicates,[98,99] should arise on the lateral surfaces of layered silicates, particularly in the case of mechanical cleavage of the layers or in topochemical reactions occurring when smectites are heated and in the presence of the strain in the Si–O–Si and Si–O–Al linkages induced by this:



Indeed the presence of oxidation-reduction centres, whose number increases with increasing heat treatment temperature of the mineral, has been established by EPR using diphenylamine, anthracene, and chloranil probes[90] (p.55). Their presence in layered silicates has been suggested, as mentioned above, on the basis of the study of the colour reactions.

VI. CATALYSIS IN THE PRESENCE OF LAYERED SILICATES

In recent years there has been a growth of interest in clays as catalysts of various processes and at the present time numerous catalytic reactions involving their participation are known. Certain examples of catalytic reactions carried out in the presence of layered silicates as well as specific reactions with participation of large molecules on fixed clay minerals are presented in Table 3. The majority of these reactions have not been investigated in the presence of other aluminosilicates, including zeolites.

Clays, acting mainly as acid catalysts, initiate a wide variety of reactions of hydrocarbons, such as cracking, β-elimination, the shifts of the methyl group, and others. The catalytic properties of clays have also been investigated in connection with the elucidation of the genesis of petroleum. For example, the conversion of n-octacosane $C_{28}H_{58}$ in the presence of montmorillonite has been investigated.[102] Heating at 375 °C led to the formation of alkanes and olefins of smaller size, the yield of n-alkanes increasing and that of

branched and cyclic alkanes and aromatic hydrocarbons falling with increase in the duration of heat treatment. The olefins formed in the cracking process underwent isomerisation, rearrangement, and cyclisation.

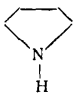
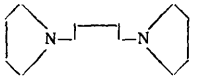
Table 3. Catalytic reactions in the presence of clays.

Field of application	Examples		Catalyst	Refs.
	starting materials	products		
Study of the genesis of petroleum. pyrolysis	Kerogen	–	Montmorillonite	[100, 101]
Ditto	Higher paraffins	–	Argillaceous rocks	[102]
"	Higher aliphatic acids	Hydrocarbons	Bentonite	[103]
Cracking of petroleum fractions	Distillates, gas oils	–	Bentonite clays	[104, 105]
Ditto	Various petroleum fractions	–	(0.5–4%) Al_2O_3/bentonite, with HNO_3	[106]
"	Higher paraffins	–	Ni-mica-montmorillinite	[107–109]
"	Gasoils, high-molecular-weight compounds in petroleum residues	–	Al-, Al-Zr-, Zr-, Al-Si-, and Si-fixed montmorillonite	[53, 55–57, 63–68, 110–115]
Hydroisomerisation of hydrocarbons	n-Pentane	Isopentane	0.2% Pd/mica-montmorillonite	[70, 116–118]
Ditto	n-Pentane	"	Beidellite	[28]
"	But-1-ene	Isobutenes	Al(Ti, Zr, Ho)-fixed montmorillonite	[119]
Hydrocracking	Higher paraffins	–	Ni-mica-montmorillonite	[67]
Ditto	n-Decane	–	Al(Ti, Zr, Ho)-fixed montmorillonite	[119]
"	Gasoil	–	Al(Zr, Si)-fixed montmorillonite	[115]
Hydropurification	Petroleum raw material	–	Ni-mica-montmorillonite	[120, 121]
Ditto	Petrol (gasoline)-ligroin fraction	–	Ni–Mo/bentonite	[122]
"	Aromatic raw material	–	1% Al_2O_3/montmorillonite	[123]
"	Mazut	–	Bentonite activated with HNO_3	[124]
"	Dibenzothiophen	Biphenyl	Mo-montmorillonite	[125]
Alkylation of aromatic compounds	Liquid benzene and toluene	Alkylbenzenes	Bentonite	[126]
Ditto	Benzene (with alcohols and olefins)	Ditto	Modified gumbrin	[127]
"	Benzene (with ethylene)	Ethylene	Silanised Al-fixed montmorillonite	[128]
"	Benzene (with propene)	Cumene	Al-fixed mica-montmorillonite	[129]
"	Benzene (with C_8–C_{18} olefins)	C_{14}–C_{24} alkylbenzenes	$Al^{3+}(In^{3+}$–$Cr^{3+})$-exchange montmorillonite	[130]
"	Benzene (with benzyl chloride)	Diphenylmethane	Vermiculite	[131]
"	Phenol (with 2-chloro-octane)	Octylphenol	Bentonite	[132]
Dealkylation	Isopropylnaphthalene	Naphthalene	Al-fixed montmorillonite	[62]
Transalkylation	Benzene + diisopropylbenzene	Cumene	Bentonite activated with H_2SO_4; fixed smectites	[133]
Disproportionation	1,2,4-Trimethylbenzene	Durene + *o*-xylene	Al-fixed montmorillonite	[134]
"	Oleic acid	Dieonic + steric acids	Ni-exchange montmorillonite	[135]
Reduction	Hex-1-ene	Hexane	Rh-phosphine/Na-hectorite	[136]
"	SO_2 (reaction with natural gas)	Elemental sulphur	Bauxite/bentonite	[137, 138]
"	CO	CO_2 + CH_4	$Ru(NH_3)_6^{3+}$/Al-fixed smectite	[139]
"	CO	Lower hydrocarbons, predominantly methane	$Ru(CO)_{12}$/montmorillonite	[140]
"	Biphenyl oxide	Benzene	Clay	[141]
Dehydrogenation	Butene	Butadiene	$Fe^{3+}(Sn^{4+})$-fluorotetrasilicate mica	[142, 143]
Intermolecular hydrogen transport	9,10-Dihydroanthracene + 1,1-diphenylethylene	Anthracene + 1,1-diphenylethane	Synthetic fluorohectorite	[144]
Ditto	Dihydroanthracene + stilbene	Anthracene + 1,2-diphenylethane	Al^{3+}-exchange montmorillonite	[144]

Table 3. (cont'.)

Field of application	Examples		Catalyst	Refs.
	starting materials	products		
Oxidation	1,1-Diphenylethylene	1,1-Diphenylethane + benzophenone	Synthetic fluorohectorite	[8]
Ditto	Leuco-bases (in coloured copy paper)	Dyes	Clays	[145]
Hydration	Ethylene	Ethanol	$Al^{3+}(Fe^{3+}, Cr^{3+}, H^+)$-exchange montmorillonite	[146]
Dehydration	Ethanol	Ethylene	Natural montmorillonite	[147]
Di- and tri-merisation	Hexene	Methylundecenes	Cu^{2+}-exchange montmorillonite	[148]
Ditto	1,1-Diphenylethylene	1-Methyl-1,3,3-triphenylindan	Cu^{2+}-exchange montmorillonite	[149]
"	*trans*-stilbene	9,10-dibenzyl-9,10-dihydroanthracene	Cu^{2+}-exchange montmorillonite	[8]
"	Indene	Dimers and trimers	Cu^{2+}-exchange montmorillonite	[8]
"	Oleic acid	Di- and tricarboxylic acids	Montmorillonite	[135]
"	Aliphatic acids in tall oil	Dimers with M.W. ≈ 560–590	Bentonite activated with H_2SO_4	[150]
Cis-trans isomerisation	Oleic acid		Cr^{3+}-exchange montmorillonite	[135]
Oligomerisation	Cyclohexene	Liquid products	$CH_3NH_4^+$-exchange montmorillonite	[151]
"	Propene	Ditto	Al-fixed montmorillonite	[152]
"	"	"	H^+-exchange montmorillonite	[153]
"	Olefins	"	0.2% Pd/mica-montmorillonite	[154]
"	Butenes	Petrol (gasoline)	Montmorillonite/kaolin	[155]
"	Isobutene	Dimer (18%), trimer (56%), tetramer (17%)	Acid clay	[156]
Polymerisation	Propene	–	Bentonite	[157]
"	Styrene	–	Acid-washed montmorillonite	[158–160]
"	Methyl methacrylate	–	H-bentonite	[161]
"	Phenol	–	$Al^{3+}(Fe^{3+}, Cr^{3+})$-exchange montmorillonite	[162]
"	Benzyl alcohol	Polyphenylenemethylene	Cu^{2+}-exchange montmorillonite	[163]
Synthesis of ethers	Olefins (with participation of intercalated water in the mineral)	–	Cu^{2+}-exchange montmorillonite	[164, 165]
Ditto	Olefin + primary alcohol	–	Al^{3+}-exchange montmorillonite	[165]
"	Primary alcohols	–	Al^{3+}-exchange montmorillonite	[163, 165]
"	Primary diols	Dioxan + triethylene glycol	Al^{3+}-exchange montmorillonite	[165]
"	Epoxyethane	Dioxan	Al^{3+}-exchange montmorillonite	[165]
"	Phenol + isobutene	*p*-t-Butylphenol	Activated clay	[166]
"	Methanol + isobutene	t-Butyl methyl ether	$Al^{3+}(Fe^{3+}, Cr^{3+})$-exchange montmorillonite	[167]
Condensation	Phenol + benzyl alcohol	Benzylphenoxide	Fluorotetrasilicate mica	[168]
Synthesis of esters	Carboxylic acid + olefins	–	$Al^{3+}(H^+, Cr^{3+})$-exchange montmorillonite	[148, 169]
Conversion of mercaptans into thioethers	Alkanethiol	Dialkyl sulphide	Al^{3+}-exchange montmorillonite	[170]
Ditto	Benzenethiol	Diphenyl sulphide	Al^{3+}-exchange montmorillonite	[170]
"	Toluenethiol	Polyphenylenemethylene	Al^{3+}-exchange montmorillonite	[170]

Table 3. (cont'.)

Field of application	Examples		Catalyst	Refs.
	starting materials	products		
Lactonisation	Cyclo-octene-carboxylic acid	1,3 + 1,4-Cyclo-octane carbo-lactone	$Al^{3+}(Co^{2+})$-exchange montmorillonite	[171]
Conversion of amines	Alkylamines RCH_2NH_2	$RCH_2.NHCH_2R$	Al^{3+}-exchange montmorillonite	[172]
Ditto	Primary cyclo-alkylamines $C_6H_{11}NH_2$	$C_6H_{11}.NHC_6H_{11}$	Al^{3+}-exchange montmorillonite	[172]
"	Secondary cyclo-alkylamines 		Al^{3+}-exchange montmorillonite	[172]
Cycloaminolysis	Acetylene	Pyridine	Bentonite activated with H_2SO_4	[173]
Conversion of methanol	MeOH	C_1–C_6 olefins, predominantly C_2–C_4 olefins	Ti-exchange montmorillonite	[174, 175]
Ditto		Ditto	SiO_2-fixed montmorillonite	[58]
"		"	Zr-fixed montmorillonite	[176]
"		$CO + H_2$	Pd(Ru, Ni, Rh)/fluorotetrasilicate mica	[177]
Conversion of synthesis gas	$CO + H_2$	Lower olefins	Fe-fixed montmorillonite	[75]

The hypothesis that aliphatic acids are precursors of the petroleum n-paraffins stimulated research into the catalytic decomposition of aliphatic acids. Thus, the decomposition of behenic acid $C_{21}H_{43}COOH$[103] on bentonite in the presence and absence of water at 200 °C yielded C_3–C_5 hydrocarbons. The total amount of saturated hydrocarbons increased with increase in the duration of heat treatment (90–760 h), while the yield of olefins fell. According to the authors,[103] the decarboxylation reaction is catalysed by the Lewis centres located on the lateral surfaces of montmorillonite, while the cracking is associated with the Brønsted acidity.

The ability of clay minerals to effect the cracking of petroleum fractions is well known.[105] However, the development of methods whereby clays can be fixed has led to new possibilities for the creation of catalysts for the conversion of high-molecular-weight compounds with a kinetic diameter >0.9 nm,[110] which are present in heavy petroleum fractions. The active catalysts for the cracking of the heavy raw material (petroleum residues, coal liquefaction products, coal tar) should have pores larger than 0.8 nm and a large internal surface.[111] The advantages of the fixation of clay minerals are manifested precisely in the cracking of large molecules. Thus the zeolite Y in the Ce-form and the fixed Ce-montmorillonite both sorb alkylbenzenes with a kinetic diameter <0.9 nm [including cumene (0.68 nm), t-butylbenzene (0.68 nm), *m*-diisopropylbenzene (0.79 nm), and tricyclodecane (0.81 nm)] and large differences between the activities of the two catalysts are not observed.[110] On the other hand, the degree of cracking of dodecahydronaphthalene (with a kinetic diameter of 1.15 nm) on fixed Ce-montmorillonite (in which the size of the inlet apertures and pores is 1.6–1.9 nm) is higher by several orders of magnitude than on the zeolite Ce-Y (with a size of the inlet apertures of 0.9 nm), on which the sorption of this compound is sterically hindered.

With decrease in the degree of cross-linking from 2.0 to 1.6 mmol of Al per gram of the Ce-montmorillonite, the activity of the fixed clay increases still further.[112] The explanation is that, under the conditions of incomplete exchange, a large amount of free space remains between the layers and is sufficient for the penetration of the reactants into the interlayer space and at the same time a certain number of cations remain and polarise the molecules of the residual water with formation of protons. In such cross-linked montmorillonite, the distance between the pillars is 1.1 to 1.9 nm, depending on the degree of cross-linking (the distances were determined from the adsorption of planar condensed aromatic compounds), while the distance between the layers is 0.8–1.0 nm. Further decrease in the degree of cross-linking to 1.25 nm lowers the thermal stability of the catalyst and decreases the total pore volume and leads to the loss of catalytic activity.

Wide-scale studies have been carried out[113] on the application to petroleum processing of montmorillonites fixed by aluminium or zirconium oligocations. However, the montmorillonite fixed by the Al_{13} oligocation lost its activity rapidly in the cracking of gasoil as a consequence of not only coke formation but also of the breakdown of its structure. With increase in temperature from 560° to 760 °C, the specific surface of the clay fixed by the Al_{13} oligocation gradually fell from 200–300 to 55 $m^2 g^{-1}$.[114] The deactivation caused by the formation of coke can be avoided by introducing into the catalyst small amounts (0.05%) of palladium and by carrying out the reaction in a stream of H_2.[134] Judging from the literature data,[134,178] by varying the conditions in the preparation of the specimens, especially from synthetic hectorite, it is possible to increase greatly the stability of the catalyst. Under optimum conditions, it is possible to obtain a catalyst whose specific surface remains fairly large (130 $m^2 g^{-1}$) even at 800 °C.[178] However, one should note that there is little information about the thermal stability of the catalysts of the new type considered here—fixed clay minerals.

The stability of the montmorillonite cracking catalyst is also increased by adding to it 30% of the zeolite HY.[115] It has been suggested that the mica-montmorillonite mentioned above be used as a component of the cracking catalyst.[109,119] There are data concerning the application of clays, including fixed clays, to the hydrocracking of paraffinic hydrocarbons, from C_{10} upwards, and the hydroisomerisation of the C_4–C_5 hydrocarbons,[67,115,119,171,175] and also as carriers of catalysts for the hydropurification of heavy petroleum raw material.[125] Molybdenum catalysts deposited on bentonite showed a much greater activity in the hydrocracking of diphenylmethane and the hydrodesulphurisation of dibenzothiophen than those deposited on Al_2O_3. However, the activity of the Mo/Al_2O_3 catalyst was much greater in the hydrogenation of 1-methylnaphthalene.

Layered silicates have been used to alkylate aromatic compounds.[126–132] The overall characteristics of the alkylation process on clays and zeolites are the same. The reaction is usually carried out[159] at temperatures up to 400 °C and pressures ranging from 20 to 50 atm in order to maintain the reaction mixture in the liquid phase. The aromatic hydrocarbon:olefin molar ratio was varied from 2:1 to 15:1 in different investigations.[127,129] The alkylation of phenol requires a somewhat lower temperature—in the range 100–200 °C,[129,132] but in each specific case the reaction conditions depend on the catalyst used and on the type of alkylating agent. In the alkylation of benzene with ethylene under flow conditions on the Al_{13}-fixed montmorillonite (384 °C, contact time 10 s, benzene:ethylene molar ratio 7:4), the degree of conversion of ethylene into alkylbenzenes (diethylbenzene and ethylben-

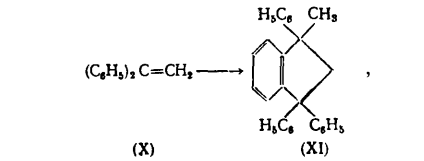
zene in proportions of 16:1) was 25.4%.[159] On montmorillonite in the H-form, treated with tetraethoxysilane, ethylbenzene was formed in 13% yield in a static system (40 atm. 200 °C, 2.5 h).[128]

Natural smectite clays (hectorite, saponite) in the cation-exchange form are used to alkylate benzene by higher olefins.[130] Under optimum conditions, the yield of the corresponding alkylbenzenes (with respect to the olefin) reaches 50%. Clays containing a cation with the highest Pauling electronegativity (Al^{3+}, In^{3+}, Cr^{3+}) are the most active. Minerals in which the cation has an electronegativity less than unity are inactive in the alkylation reaction. In the alkylation of phenol with chloro-octane (150–155 °C, 20 h) in the presence of natural bentonite, the yield of octylphenol (with respect to the alkane) reaches 92%.[132] Overall, comparative tests of the zeolitic catalysts H–ZSM and of fixed bentonite[179] showed that the latter is most suitable as the catalyst of the alkylation of benzene by olefins.

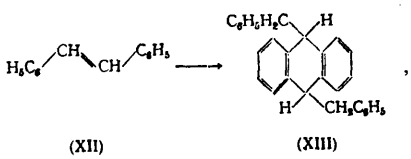
Dealkylation of isopropylnaphthalene[62] has been investigated in the presence of the Al-fixed montmorillonite dehydrated by the vacuum sublimation of a frozen specimen or by drying the specimen in air at room temperature. The reaction was carried out in a flow reactor at 300–400 °C and with a contact time of 0.6–3.6 s. The initial activities of the two specimens were similar (conversion 90–100%), but the catalyst dried by sublimation proved to be much more stable, The specimen dried in air rapidly lost its activity as a consequence of coke formation.

The transalkylation[124,163] and disproportionation[125,134] reactions of aromatic hydrocarbons have been carried out on bentonite activated by H_2SO_4 and on fixed smectites. A number of other catalytic reactions of hydrocarbons in the presence of clays are also known: hydrogenation,[136] dehydrogenation,[142,143] hydration of olefins,[146] oxidation,[8,45] etc.

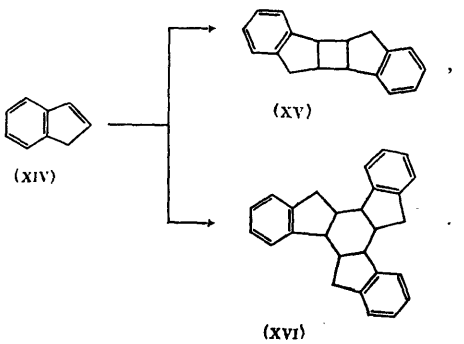
Studies of the dimerisation, oligomerisation, and polymerisation of olefins in the presence of layered silicates are of interest. As in the case of cracking, the use of layered and especially fixed silicates in these reactions makes it possible to introduce into the reaction or obtain large molecules:[8,149]



(X) (XI)



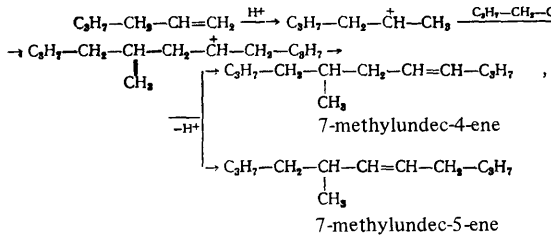
(XII) (XIII)



(XIV) (XV) (XVI)

For example, 1-methyl-1,3,3-triphenylindene (XI), whose molecule contains four aromatic rings, has been obtained[149] by dimerising 1,1-diphenylethylene (X) on Cu^{2+}-montmorillonite. The even larger 9,10-dibenzyl-9,10-dihydroanthracene (XIII) molecule is formed on the same catalyst from *trans*-stilbene (XII).[8] The dimerisation and especially the trimerisation of indene (XIV) leads to compounds (XV) and (XVI),[8] which cannot be obtained in comparatively narrow pores and cannot emerge from pores of moderate size and coke is gradually formed. Admittedly, one cannot rule out the possibility that such molecules can be assembled from the monomers on the lateral surface of the smectite crystal carrying acid centres of different strengths.

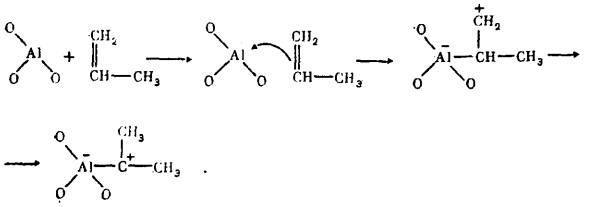
The mechanism of the dimerisation of olefins can be represented as follows in relation to hex-1-ene:[148]



7-methylundec-4-ene

7-methylundec-5-ene

Evidently, the oligomerisation of olefins under mild conditions can also be considered from the standpoint of the proton-donor mechanism. However, according to Occelli et al.,[152] the oligomerisation of propene on a fixed bentonite at temperatures up to 400 °C proceeds with participation of Lewis acid centres, which predominate on the surface even at temperatures above 300 °C. In this case, the reaction begins with the interaction of a highly active Lewis acid centre with a propene molecule and the formation of a stable π-complex. Electron transfer to an unoccupied orbital of the aluminium atom leads to the appearance of a σ-complex in which the propene fragment carries a positive charge:



After the addition of a propene molecule to this carbonium ion, chain propagation begins.

The elucidation of the cause of the activity of clays in polymerisation reactions[157–160] was assisted by a study of the interaction of leuco-bases with clay minerals.[92] This investigation resulted in the development of a donor–acceptor mechanism of the interaction of organic compounds with clays,[86,92,180] an example of which is presented in Section V.

The activity of montmorillonite in the styrene polymerisation reaction is appreciably suppressed after treatment with polyphosphates,[160] which is explained, as for the colour reactions (see Section V), by the presence on the lateral surface of electron-accepting (Lewis) centres consisting of aluminium atoms in an octahedral coordination. Since the polymerisation reaction has features characteristic simultaneously of free-radical and ionic mechanisms, it has been suggested[160] that electron transfer from the adsorbed styrene to aluminium results in the appearance of a radical-cation, which is rapidly converted into a dimer. Both the radical-cation and its dimer initiate the process, but the polymerisation itself proceeds via a cationic mechanism. Alcohols and amines inhibit

the polymerisation: being stronger Lewis bases, they are adsorbed preferentially.[158]

On the other hand, it has been suggested[181] that Brønsted and not Lewis acidity is responsible for the initiation of the polymerisation. However, whereas alkaline treatment suppresses the polymerisation completely, the adsorption of triphenylmethyl chloride on the Lewis centres on the lateral surfaces only reduces the yield of the polymer. It would therefore be an oversimplification to relate the activity of montmorillonite to its Lewis or Brønsted acidity only.

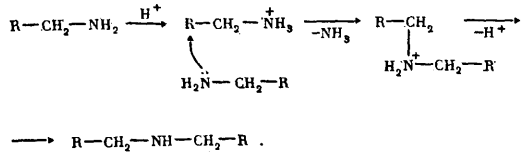
Various reactions of olefins, alcohols, thiols, and amines on layered silicates at low temperatures have been studied recently.[182] The reactions of olefins with water and alcohols afford ethers, those with carboxylic acids give rise to esters, and those with thiols produce thioethers (sulphides). Olefins do not react with amines on layered silicates.

It is noteworthy that the formation of an ether from an olefin and water requires an intermediate stage in which an alcohol is formed.[164] This reaction takes place with participation of the intercalated water after the exhaustion of which the reaction ceases; the catalyst cannot be regenerated. Smectites containing an exchange cation with the maximum polarising effect (Al^{3+}, Fe^{3+}, Cr^{3+}) exhibit the highest activity. However, the greatest selectivity in the formation of ethers has been attained on Cu^{2+}-exchange montmorillonite. For each cation, there is an optimum content of the intercalated water for which the yield of the ether is a maximum. The optimum $Cu:H_2O$ ratio for Cu^{2+}-montmorillonite is 1 : 12.[171]

The reactions of alcohols on layered silicates, which proceeds via an acidic mechanism, lead to the formation of ethers, alkenes, and alkene dimers.[163] Primary alcohols then give rise preferentially to ethers, secondary alcohols yield mainly alkenes, while tertiary alcohols give rise to alkenes and their oligomers exclusively. The fixation of montmorillonite and beidellite by the Al_{13} oligocation (d then increases to 1.8 nm) leads to a sharp fall in their catalytic activity in the reaction involving the formation of ethers from alcohols and of esters from an olefin and a carboxylic acid.[27]

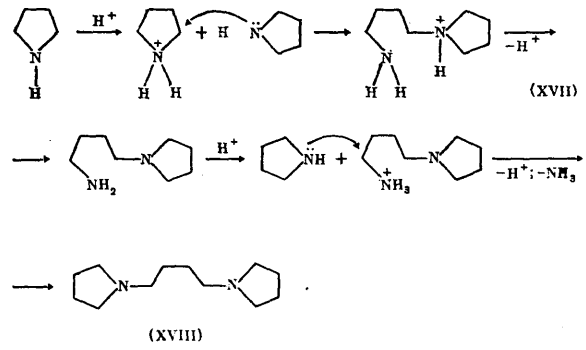
The reaction of benzyl alcohol on Cu^{2+}-montmorillonite takes place in an interesting manner:[62,163] polyphenylenemethylenes containing between 10 and 100 phenylenemethylene fragments are formed. The reaction of an aromatic thiol is of the same type.[170] The dimerisation of epoxyethane on Cu^{2+}-montmorillonite leads to the formation of a cyclic ether—dioxan.[109,182]

The reaction in which secondary amines are formed from primary anions on Cu^{2+}- or Al^{3+}-montmorillonite[172] has also been considered from the standpoint of a proton mechanism:



The formation of alkenes from amines was not then observed.

The rate of conversion of 2-alkylamines and cyclic amines is higher than that of 1-alkylamines (aniline is known to form complexes with clays,[172] but the nucleophilic substitution reaction does not occur). Cyclic secondary amines, for example, pyrrolidine, also split off ammonia in the presence of the Cr^{3+}-exchange montmorillonite, but in this case three amine molecules are involved in the reaction:[172]

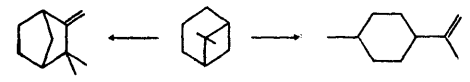


(XVII)

(XVIII)

With increase in reaction time, the yield of compound (XVIII) increases and that of compound (XVII) falls, which indicates the intermediate character of the latter. The formation of piperidine and pyridine from acetylene and ammonia has been observed on bentonite activated with H_2SO_4.[173]

It is noteworthy that certain compounds react on layered silicates in a way which is different from that on zeolites. For example, α-pinene affords up to 20% of camphene and a large number of polymers on layered silicates, 50–62% of camphene has been obtained under industrial conditions on clays treated with acid, while on a synthetic zeolite the main product is dipentene:[183]



Camphene α-Pinene Dipentene

The "chemistry of C_1 compounds", which is based on the reactions of methanol and the synthesis gas, has acquired considerable importance in research and for practical purposes in all countries during the last decade. The possibility of using layered silicates as catalysts in this field has therefore been frequently investigated. For example, olefins, mainly having the C_2–C_4 composition, have been obtained from methanol in high yields on montmorillonites—both containing different exchange cations and fixed.[174–177] In this reaction too, the activity of the catalysts is related to their acidity. Preliminary treatment of the clay which enhances its acid properties, such as for example, the exchange of the Na^+ and Ca^{2+} cations for Ti^{4+} ions, greatly increases the degree of conversion of methanol.[174] Certain questions of the mechanism of the formation of higher olefins from methanol on zeolites have been examined in detail.[184] The similar nature of the active centres on zeolites and layered silicates (see Section V) suggests that the reactions on the latter proceed via the same mechanism.

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The data presented in this review show that the uses devised in recent years for layered silicates, in particular clays, in the preparation of catalysts have greatly expanded the scope of catalysis, mainly acid–base catalysis. This is due to the ready availability and low cost of the widely occurring natural raw material, the thermal stability of fixed clays, and the possibility of accelerating with their aid the reactions of large molecules. The latter is especially important at the present stage of development of the chemical, petrochemical and coal-chemical industry, which requires the creation of a

waste-free ecologically clean industry and hence the development of processes for the utilisation of the heavy residues remaining after the processing of different types of organic raw material containing large molecules.

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Metal Complex Catalysis of Electrode Processes

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A new field of application of metal complexes for the acceleration of electrode processes is examined. The general principles of the design of metal complex electrocatalytic systems are analysed and the results of studies carried out during the last 10 years on the electrochemical reduction and oxidation of various organic and inorganic substrates are surveyed.
The bibliography includes 177 references.

CONTENTS

I. Introduction 129
II. General principles 129
III. The main electrochemical reactions catalysed by metal complexes 130

I. INTRODUCTION

During the last 30 years, considerable advances have been made in metal complex catalysis (MCC) and have had a strong influence also on other types of catalysis; heterogeneous enzyme catalysis and electrocatalysis. This influence is due to the high theoretical level of understanding of the processes undergone by the substrate in the coordination spheres of metal complexes—in particular, in the case of homogeneous MCC, where it has been possible in many cases to elucidate the sequence of the elementary reactions, to isolate or identify spectroscopically the intermediate compounds, to follow the changes in the oxidation states of the metals during the catalytic process, and to achieve a quantum-chemical description of the character of the bond between the substrate and the metal.[1,2]

Together with the fundamental importance of MCC for the generation of fundamental ideas referring to catalysis as a whole, the practical advantages which it can ensure play a significant role. This applies in the first place to the comparatively mild reaction conditions in solution (low temperature and pressure), low sensitivity to impurities and catalytic poisons, the accessibility of the active centres to the interaction with the substrate, and finally the possibility of controlling the catalytic system by altering the ligand environment of the metal complex and the composition of the medium. In many cases, homogeneous catalysts are superior to heterogeneous catalysts as regards selectivity, being at the same time much more readily available.

The principles of MCC can be readily transferred to the catalysis of electrochemical reactions. In particular, metalloporphyrins have been used successfully to carry out electrocatalytic hydrogen reduction reactions in fuel cells in order to replace or reduce significantly the consumption of expensive metals.[3] However, the application of MCC in electrosynthesis, which has developed most recently, is of greatest interest. One can point out a series of factors which make the combination of MCC with electrochemistry particularly attractive to specialists in both fields. These are in the first place the possibility of replacing at the electrode strong oxidants and reductants, which are frequently expensive and difficult to obtain and furthermore contaminate the reaction mixture by their conversion products. By carrying out a redox reaction at the electrode, it is possible to influence within wide limits its rate by regulating the electrode potential, and to ensure the transfer of any number of electrons without altering the composition of the medium, which is especially important in many-electron reactions. The possibility of lowering the overpotential at the electrode and of increasing the current density by means of MCC are in their turn attractive to electrochemists. Finally, special mention should be made of the fact that MCC can ensure the occurrence of chemical reactions which are altogether impossible in the absence of metal complexes, for example the reduction of nitrogen or carbon monoxide. Furthermore, one should add that the modern methods for the investigation of electrode processes, namely various types of polarography, cyclic voltamperometry, and various pulse methods make it possible to achieve a fairly complete description of the mechanism of the catalysis when combined with electrolysis at a controlled potential and spectroscopic methods.

The statement of the well known electrochemist Baizer[4] that there are unlimited possibilities for an investigator working at the junction of organic chemistry, electrochemistry, and catalysis is fully applicable to metal complex electrocatalysis (MCE). Investigators can use pure methods for the introduction and removal of electrons, procedures for the deposition of potential catalysts on electrode matrices, the advantages of adsorption on electrodes which depends on the electric field, a large set of solvents, and, if necessary, supporting electrolytes which exert a specific influence on the electrode processes and the behaviour of intermediate species in solution.

The trend towards an increase in the number of studies involving the use of metal complexes in electrocatalysis observed in recent years requires systematic treatment of the accumulated data in this essentially new field. It is necessary to understand the methodology of the selection of metal complex electrocatalysts, the general principles of their functioning, and the possibilities and prospects for their use in electrochemical reactions of various substrates. This review is in fact devoted to the consideration of these questions.

II. GENERAL PRINCIPLES

In terms of the mechanism of their action, metal complex catalysts of electrosynthesis can be divided into two main groups. The first includes metal complexes whose coordination spheres remain unchanged throughout the catalytic cycle and electron transfer takes place via an outer sphere mechanism without the formation of an intermediate complex between the substrate (A) and the catalyst (the redox pair P/Q):

$$\begin{gathered} P+e \rightleftharpoons Q, \\ Q+A \rightleftharpoons P+B, \\ B \rightarrow C\ . \end{gathered}$$

It has been suggested that this type of MCE be called redox catalysis.[5] The functions of the redox catalyst (other names: redox transferring agent, mediator) consist in electron transfer from the electrode to the substrate, after which the primary product B of the reduction of the substrate is converted into the final product C already in the course of the chemical reaction. When B is rapidly and irreversibly converted into C, the substrate may be reduced under the conditions of homogeneous electron transfer in the direction opposite to the standard potential drop ($E^0_{P/Q} > E^0_{A/B}$),[6] which greatly extends the scope of redox catalysis. Evidently a gain is achieved using redox catalysts only when they are capable of being rapidly regenerated at the electrode and with high yields at potentials more positive than those of the direct electrochemical reduction of the substrate or less positive than the potentials of its direct electrochemical oxidation, are stable, and can interact rapidly with the substrate. Thus this type of MCE can be usefully employed if, by restorting to homogeneous electron transfer, one increases the rate of the process as a whole by transferring the process to the bulk of the solution and by reducing the overpotential of the electrochemical reaction and also if substrates for which homogeneous redox reactions occur for one reason or another at higher rate than heterogeneous reactions participate in the process.

The second group of catalysts includes metal complexes with the participation of which electron transfer from the electrode to the substrate takes place via an inner sphere mechanism with formation of an intermediate complex between the catalyst and the substrate (PA or QA). The mechanism of the action of these catalyats can be represented in a simplified form by the following schemes:

$$\left.\begin{array}{l}\overrightarrow{P + A \rightleftharpoons PA}\\ PA \xrightarrow{e} PB \rightarrow P + C\end{array}\right|$$

or

$$\left.\begin{array}{l}\overrightarrow{P + e \rightleftharpoons Q}\\ Q + A \rightleftharpoons QA\\ QA \xrightarrow{e} QB \rightarrow P + C\end{array}\right| .$$

Since the reactions of the substrate in the coordination sphere of the metal complex assume the main role in the catalytic cycle, this type of MCE can be usefully defined as coordination electrocatalysis. The electrochemical stage and the chemical reaction of the substrate are coupled with participation of the catalyst–substrate complex and the function of the catalyst consists in the binding and activation of the substrate in the coordination sphere of the metal complex as a result of which the reactivity of the substrate in the electron exchange reaction with the electrode increases. In contrast to redox catalysis, in coordination MCE, P or Q must be coordination-unsaturated or must contain ligands which are kinetically labile in substitution reactions. This is essential for the formation of the intermediate complexes PA and QA.

The choice of a specific metal complex for coordination MCE is appreciably facilitated by the availability of extensive information on the complex formation reactions and activation of substrates which are kinetically inert in redox reactions.[1,2] Having chosen a suitable metal complex which binds the substrate and activates it in its coordination sphere, one can proceed to the solution of practical problems in the coupling of the electrode and chemical reactions. This strategy is evidently idealised but in the subsequent description of this approach it will be illustrated by a number of examples.

In coordination MCE, the metal complex can be immobilised on the electrode surface, for example, by adsorption and special fixing methods,[7] or can be present in the bulk of the solution. The electron exchange between the electrode and the catalyst–substrate complex can then take place either directly or with participation of redox transferring agents. In particular, if the reaction centre in the immobilised coordination catalyst exchanges electrons slowly with the electrode, then the efficiency of this process can be increased by the additional immobilisation on the electrode surface of a redox transferring agent capable of rapid electron exchange both with the electrode and with the reaction centre. As will be shown below, this approach, which has been developed in bioelectrocatalysis for the coupling of enzymes in electrochemical reactions,[8] can be used successfully also in coordination MCE.

In conclusion, we may note that coordination MCE is in fact the only method for the involvement in electrochemical reactions of substrates whose direct oxidation-reduction at the electrode is difficult or does not occur at all. Attention will therefore be concentrated in the present review on precisely this type of MCE.

III. THE MAIN ELECTROCHEMICAL REACTIONS CATALYSED BY METAL COMPLEXES

1. Dehalogenation of Organic Halides

The problem of the dehalogenation of organic halides RX, where R = aryl or alkyl and X = Cl, Br, or I, is of not only theoretical but also of applied importance, because many halides accumulate in the waste from industrial organic synthesis. The direct electrochemical reduction of alkyl and aryl halides is usually carried out at potentials more negative than −1.5 V.†[4] The pattern changes significantly when the complexes of certain transition metals capable of reacting with RX to form more readily reducible compounds are introduced into the electrolyte solution. The reductive dehalogenation of RX can then be performed at considerably more positive potentials, usually at the potentials of the regeneration of the metal complex active in relation to RX. The complexes catalytically active with respect to RX can be arbitrarily divided into three groups: the phosphine, tetra-azamacrocyclic, and polypyridyl complexes. We shall consider each of these groups.

The tetraphosphine complexes of zerovalent nickel $NiPn_4$, electrochemically generated by the two-electron reduction of Ni^{2+} or NiX_2Pn_2 in the presence of an excess of phosphine Pn, catalyse the electrochemical reduction of RX (R = alkyl or benzyl) and ArX (Ar = aryl) with formation of a mixture of the corresponding hydrocarbons (RH or ArH), dimerisation products (R–R or Ar–Ar) and, in the case of alkyl halides, also the alkenes R(−H).[9–11] The reduction takes place at Hg, Pt, Au, or carbon glass cathodes in a diaphragm electrolyser in various solvents [EtOH, tetrahydrofuran (THF), MeCN, etc.]. The ratio of the products depends significantly on the nature of the solvent but not of the electrode. Thus, in the catalytic electrochemical reduction of ArX in an alcoholic medium, the only product is the corresponding ArH, while in THF or in its mixtures with hexamethylphosphoramide (HMP) the product is a mixture of ArH and Ar–Ar, the

† All the potentials are quoted in this review relative to the aqueous saturated calomel electrode.

material yield of biaryl increasing to 70–95% with increase in the HMP content.[9] The electroanalytical study of this reaction permitted the conclusion that the mechanism of the dehalogenation of aryl halides can be represented as schematically as follows:[9]

$$Ni^{2+} \xrightarrow{2e;\ Pn} NiPn_4 \xrightarrow{ArX} ArNiXPn_2 \xrightarrow{2e;\ H^+} Ar^- + NiPn_4,$$
$$Ar^- \xrightarrow{H^+} ArH$$
$$Ar^- + ArNiXPn_2 \rightarrow Ar{-}Ar + X^- + NiPn_4.$$

As a result of the oxidative addition of RX to $NiPn_4$, the intermediate formation of the organonickel σ-derivative $RNiXPn_2$, the stability and further reaction pathways of which depend significantly on the nature of the solvent and the halide, has also been postulated for alkyl halides.[10] Tributyl- and triphenyl-phosphines[9,10] and the diphosphines of the type of bis(diphenylphosphino)ethane (dppe) [12] are used in this reaction.

The study of the mechanism of the electrochemical reduction of 1-iodobutane, 1-iodo-2,2-dimethylpropane, benzyl chloride, and PhBr at an Hg cathode in MeCN in the presence of catalytic amounts of $[Ni(PPh_3)_2(MeCN)_4]^{2+}$ and an excess of PPh_3 led to the conclusion[13] that the active species in relation to RX is also the electrochemically generated $Ni(PPh_3)_4$ and that the subsequent reaction of $RNiX(PPh_3)_2$ (I), formed as a result of oxidative addition, depends on the nature of the organic halide and proceeds in accordance with one of the possible schemes

$$(I) \xrightarrow{e} [RNi(PPh_3)_2X]^- \rightarrow R{-}R + Ni(PPh_3)_4 + X^-,$$
$$(I) \rightarrow Ni(PPh_3)_3X + R^{\cdot} \rightarrow R{-}R + RH + R(-H)$$

via a hydride complex i.e.

$$(I) \rightarrow R(-H) + [Ni(PPh_3)_2(H)X] \rightarrow Ni(PPh_3)_3X + RH + H_2$$

with subsequent electrochemical regeneration of $Ni(PPh_3)_4$. The same complex can promote the electrochemical reduction of allyl halides in MeCN to hexa-1,5-diene with a current yield of 85–95%.[14] The formation of the nickel(I) π-complex $(\pi\text{-}C_3H_5)Ni(PPh_3)Cl$, whose subsequent one-electron reduction is accompanied by the cleavage of the C–Ni bond with regeneration of the catalyst and the formation of the anion X^- and the radical $C_3H_5^{\cdot}$, dimerising with formation of hexadiene, has been proposed as an intermediate in the oxidative addition of the substrate to $Ni(PPh_3)_4$. An important condition for the occurrence of this electrocatalytic reaction is a tenfold excess of PPh_3 relative to Ni^{2+}, which is the initial ion for the preparation of $Ni(PPh_3)_4$.

Together with the diphosphine complexes of nickel, the product of the reversible one-electron reduction $[Rh(dppe)_2]^+$ also exhibits a catalytic activity in the dehalogenation reaction.[15] In the absence of the substrate, the $RH(dppe)_2$ generated electrochemically at the Hg cathode reacts with the solvent [dimethyl sulphoxide (DMSO), MeCN, etc.] to form the hydride $RhH(dppe)_2$, while in the presence of cyclohexyl chloride, a mixture of cyclohexane and cyclohexene is formed. The detection of dicyclohexylmercury as a side product indicates that the reaction proceeds via the intermediate formation of the free cyclohexyl radical.

The phosphine complexes of zerovalent nickel can also be used to carry out more complex reactions with participation of RX. For example, it has been shown[16] that, in *N*-methylpyrrolidinone or a THF–HMP mixture (Au-cathode), the complex $[Ni(Pn_2R'X]^-$, where R′ = ethylene, propene, or styrene and X = Cl, Br, or I, generated by the reduction of Ni^{2+} in the presence of a threefold excess of Pn = PPh_3 and an alkene, reacts with halogenobenzenes to form the corresponding arylalkenes via the mechanism (for example, when R′ = C_2H_4)

$$NiPn_2X_2 + R' \xrightarrow{2e} [NiPn_2R'X]^- \rightleftharpoons \text{«PhNiX»} \xrightarrow{Et_3N} PhCH{=}CH_2 + Ni(0) + Et_3NHX$$

Olefins are arylated as a result of the reversible oxidative addition of PhX with formation of the organonickel complex "PhNiX" of unknown structure, which decomposes irreversibly to form the arylalkene. The process becomes catalytic only in the presence of a base (Et_3N), which apparently promotes the elimination of HX.

Another example of the use of RX for the preparation of more complex products is the electrocatalytic synthesis of arylacetic and arylpropionic acids.[17] These acids are formed as a result of the electrochemical reduction of the corresponding benzyl halides at an Hg cathode in a CO_2-saturated aprotic medium (mixtures of THF with HMP or *N*-methylpyrrolidinone) in the presence of catalytic amounts (10%) of diphosphine complexes of zerovalent nickel or zerovalent palladium. The products are formed via the following proposed mechanism (L = diphosphine):

$$ML_2 \xrightarrow[-L]{RX} RMXL \xrightarrow[-X^-]{2e} RML^- \xrightarrow{CO_2;\ L} RCO_2^- + ML_2$$

The material yield of acids is 20–50% and bibenzyls are formed as side products.

Another group of complexes catalysing the electrochemical reduction of RX consists of square planar nickel(II) and cobalt(II) complexes with tetra-azamacrocycles (L) or Schiff bases. Thus it has been shown[18] that the complexes NiL^{2+} in an aprotic medium [MeCN, dimethylformamide (DMF), DMSO, etc.] undergo reversible one-electron reduction to the stable complexes NiL^+, which undergo an oxidative addition reaction with RX (2-bromo-octane, 2-bromo-2-methylheptane, etc.) to form the organonickel compounds $[RNi(L)Br]^+$ (II), whose subsequent fate depends on the nature of R. For primary RBr, the dehalogenation products RH, R(–H), and R–R are formed as a result of the competing reactions

$$(II) + RBr \rightarrow R{-}R$$

and

$$(II) \xrightarrow{e} R^- \xrightarrow{H^+} RH),$$

while secondary and tertiary RBr are dehalogenated exclusively via the radical mechanism[18]

$$((II) \rightarrow R^{\cdot} \rightarrow RH + R(-H) + R{-}R)$$

The dehalogenation reaction is catalytic and takes place at potentials corresponding to $E^0(NiL^{2+/+})$. It is of interest to note that the introduction of any substituents into L shifts $E^0(NiL^{2+/+})$ to the anodic region, the maximum effect being generated by substituents at the N atoms of the ligand, which makes it possible to lower the RBr reduction potentials down to −1 V.[18] The main products of the dehalogenation of RBr in the presence of nickel(II) complexes of Schiff bases are the corresponding dimers R–R, which shows that the reaction proceeds mainly via a radical mechanism.[19]

The tetra-azamacrocyclic complexes CoL^{2+} [20,21] and the cobalt(II) complexes of Schiff bases[22] exhibit an analogous catalytic activity in the dehalogenation of RX at the potentials of the Co(II/I) redox transition. For example, in the dehalogenation of BuX (X = Cl or Br) in the presence of the electrochemically generated bis(salicylideneiminato)cobalt(I) $[Co(salen)]^-$, the main product is 2-methylpropene. The formation of alkylcobaloxime (sic) [BuCo(salen)] as a side product indicates, according to the authors,[22] the intermediate formation of the butyl radical.

The formation of alkylcobaloximes (sic) [RCo(salen)] in the reaction of $[Co(salen)]^-$ with RX has been used for the electrocatalytic carboxylation of organic halides.[23] Electrolysis of alkyl and benzyl chlorides [R = $PhCH_2$, $Ph(CH_3)CH$, $PhCH{=}CHCH_2$, $CH_3CH{=}CHCH_2$ etc.] at the Hg cathode in the presence of the [Co(salen)] catalyst in a THF–HMP mixture

saturated with CO_2 at atmospheric pressure leads to the formation, after the hydrolysis of the catholyte, of the carboxylic acids RCO_2H in a material yield of 50–97%. In a moist solvent with an H_2O content of $(1–5) \times 10^{-2}$ M, the yield of acids falls somewhat, simultaneously with the appearance in the product of the corresponding RH and R–R. The formation of acids is not observed for aliphatic halides (bromopropane) or bromostyrene, but acids are formed from aryl halides after the replacement of the cobalt complex by $Ni(Ph_3P)_4$. It has been suggested[23] that the formation of acids can be described by the following scheme:

$$[Co\,(salen)] \overset{e}{\rightleftharpoons} [Co\,(salen)]^- \xrightarrow{RX} [RCo\,(salen)] \xrightarrow{2e;\ CO_2} RCO_2^- + [Co\,(salen)]$$

The reaction proceeds either via the intermediate formation of an adduct of CO_2 with alkylcobaloximes or via the attack on CO_2 by the carbonium ion formed on dissociation of [RCo. .(salen)]. In the light of these data, it is appropriate to mention a study[24] in which it was shown that the two-electron multistage reduction of alkylcobaloximes [RCo(dmg)Py] (where R = alkyl or benzyl, dmg = dimethyl glyoximate, and Py = pyridine) is accompanied by the formation of a dealkylated cobalt(I) complex whose two-electron reoxidation regenerates the initial alkylcobaloxime in a material yield of 60–95%. In the case of optically active groups R, the oxidation-reduction process involving the initial complex is accompanied by the complete inversion of configuration. A mechanism of the cleavage of the Co–R bond in the reduction of alkylcobaloximes, according to which the axial group R, split off in the form of R$^\cdot$ or R$^-$, remains reversibly bound to cobalt(II) or cobalt (I) complexes as a result of its transfer to the nitrogen atom of the equatorial dmg ligand, has been proposed on the basis of the data obtained. It is quite possible that, in the course of the synthesis of carboxylic acid,[23] the reduction of [RCo(salen)] is also accompanied by the transfer of R to the axial ligand with the simultaneous liberation of a coordination site for a CO_2 molecule. After the coordination and activation of CO_2, the reverse transfer of R takes place, but this time to a CO_2 molecule with formation of a carboxylate ion.

The complexes, which are structural models of vitamin B_{12}, can apparently be used also for involving alkyl halides in other interesting reactions, for example, in reductive cross-coupling. Thus the electrolysis of a mixture of ethyl iodide and acrylonitrile in MeCN at a carbon electrode polymerically modified by the 3,5-diaminobenzoyl derivative of vitamin B_{12} results in the selective formation of valeronitrile.[25] The complex $Ni(teta)^{2+}$ (where teta = hexamethyltetra-azacyclotetradecane) catalyses the electrochemical dehalogenation of RX (for example, 1-bromo-octane) with formation of RH (30%), R–R (45%), and R(–H) (20%).[26,27] After the additional introduction of activated olefins (CH_2 = CHY, where Y = Ar, CN, CO_2Et, etc.) into the catholyte together with RX, the cross-coupling products RCH_2CH_2Y are found to be formed. This reaction is not catalytic, since the complex $[Ni(teta)X_2]^+$ formed is electrochemically inactive.[26]

The third group of compounds catalysing the reductive dehalogenation of RX includes the polypyridyl complexes of Group VIII metals. It has been shown[28,29] that $Co(bipy)_3^{2+}$ (where bipy = 2,2′-bipyridyl) in MeCN catalyses the reductive dimerisation of allyl halides to hexa-1,5-diene. The hexadiene is formed at the redox potentials of $Co(bipy)_3^{2+/+}$, i.e. at potentials more anodic by 1.2 V than the potential of the reduction proper of allyl chloride at a platinum electrode.[29] The oligomers $-[CH_2CH(CH_2Cl)]-_n$ are formed together with the hexadiene. The same reaction can be carried out also in an aqueous medium.[30]

The formation of the hexadiene has likewise been observed in the electrochemical reduction of allyl bromide in MeCN in the presence of $Ni(bipy)_3^{2+}$ and a tenfold excess of the ligand.[31] Alkyl and aryl bromides are dehalogenated with formation of mainly the dimers R–R in DMF in the presence of the $Ni(phen)_3^{2+}$ catalyst (where phen = 1,10-phenanthroline).[32]

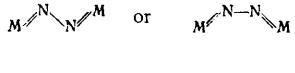
The electrochemical dehalogenation of alkyl and aryl halides can be carried out at a cathode subjected to preliminary modification with the reduction products of the metal complexes. Thus 1-bromo-octane is dehalogenated in DMF in the electrolyser fitted with aluminium electrodes but without a diaphragm, where the cathode is coated by an iron-containing deposit.[33] The dehalogenation of RBr is then achieved at potentials more anodic by 0.9 V than at the aluminium cathode. Under analogous conditions, a cathode coated by the deposit formed in the electrochemical reduction of $Ni(acac)_3$ catalyses the dehalogenation of aryl and benzyl halides.[34]

1,1-Dibromo-2-phenylcyclopropane is dehalogenated with formation of 1-bromo-2-phenylcyclopropane (90%) and phenylallene (10%) in the presence of catalytic amounts of $CrCl_3$. The reduction is carried out at a lead cathode in DMF at the potentials of the $Cr^{3+/2+}$ redox transition, which are more annodic by 2 V than the potentials of the electrochemical reduction proper of the halide.[35] Examples of other reactions involving the electrodehalogenation of organic halides catalysed by metal complexes can be found in Tanaka's review.[36]

2. Reduction of Molecular Nitrogen and Nitric Oxide

The problem of the fixation of nitrogen under mild conditions has attracted the constant attention of investigators during the last 20 years. Although the biological fixation of nitrogen has long been known, the mechanism of this most important reaction remained unknown until recently. The attempts to find simple chemical reactions permitting the reduction of nitrogen to ammonia close to biological conditions have been frequently undertaken, but they encountered difficulties associated with the necessity to rupture the exceptionally strong triple bond in nitrogen (920 kJ mol^{-1}).

Theoretical study has shown[37] that in protic media the most economical pathway (in the sense of energy expenditure) involves the activation of nitrogen in the linear dinuclear complex M...N=N...M, which tends to weaken appreciably the N≡N bond. The best catalytic properties should be manifested by metal ions with the d^3 electronic configuration, for example, Mo^{3+} and V^{2+}. With their participation, the many-electron reduction of nitrogen to N_2H_4 and NH_3 can take place without the intermediate formation of the thermodynamically extremely unfavourable diimide N_2H_2 under conditions with a more uniform distribution of energy among different stages. Such equalisation of the energy relief is achieved by the stabilisation of the intermediates formed in the reduction of nitrogen, as a result of the "conjugation" effect, i.e. the overlap of the *d* orbitals of the metal and the *p* orbitals of nitrogen, for example, in hydrazine derivatives



which have a planar configuration.

The creation of a metal complex electrocatalyst should include the search for a suitable complex $M(d^3)$ capable of activating nitrogen via the coordination mechanism described above and of reacting either directly at the electrode or with participation of a suitable catalytic transferring agent.

The first attempts to set up electrochemical systems for the reduction of nitrogen were based on the use of the nitrogen-fixing hydroxide system $Ti(OH)_3$–Mo(III) in a methanolic alkaline solution. In this system, molybdenum(III) played the role of a catalyst activating nitrogen and titanium(III) played the role of the reductant.[38] The available information about the involvement of a large number of Ti^{3+} ions in electron transfer to the active centre[38] permitted the hope that it would be possible to use Ti^{3+} as the catalytic transferring agent in amalgam or electrochemical reduction. Indeed the introduction of sodium amalgam into the system made it possible to increase appreciably the yields of N_2H_4 and NH_3,[39,40] the formation of nitrogen fixation products being observed already at 20 °C, while in the absence of the amalgam the reaction was carried out at temperatures above 80 °C. The relatively slow reduction of hydrazine in this system and the kinetics of the accumulation of ammonia showed that the fixation products are formed via parallel pathways.[40]

The results obtained in the amalgam reduction of nitrogen made it possible to proceed to direct electrochemical reduction at a mercury cathode in the same system.[41] It was found that the maximum yield of products is attained at a current density of 0.5 mA cm^{-2} or a potential of −1.86 V, i.e. under the conditions for the formation of sodium amalgam on the electrode.[42] At more positive potentials, the rate of reaction decreased exponentially with decrease in the absolute potential, in conformity with the slow discharge theory, while at more cathodic potentials the absorption of charged hydroxide species was hindered. When the mercury cathode was replaced by a rotating amalgamated copper electrode (3000 rev min^{-1}), the electrochemical nitrogen reduction reaction became selective with respect to hydrazine. This was explained[43] by the short contact times between the activated species and the electrode surface as a consequence of which the transfer of six electrons with formation of ammonia became less probable than the four-electron reduction of nitrogen to hydrazine.

The study of the electrochemical behaviour of titanium(III) and titanium(IV) chlorides in methanol made it possible to discover conditions under which the solution remained homogeneous even at a relatively high alkalinity (guanidine buffer, $pK = 13.6$) and titanium(IV) was reduced to titanium(III).[44] The introduction of molybdenum(III) did not affect the homogeneity of the solution. The formation of N_2H_4, catalysed by this system, in electrolysis in a diaphragm electrolyser (a mercury pool at the bottom serving as the cathode at a nitrogen pressure of 30 atm) began at −1.6 V, which corresponded to the half-wave potential for the reduction Ti(IV) + e → Ti(III). The composition of the medium had a significant influence on the rate of reaction.[45,46] The increase in the concentration of alkali as a result of the evolution of hydrogen at the cathode led to a decrease in the rate of formation of N_2H_4, which, however, increased again to the previous value after the introduction of water. It was assumed that the active species in the reduction of nitrogen were heteronuclear titanium(III) and molybdenum(III) complexes; furthermore, the titanium(III) complexes might have played the role of electron transferring agents. The catalytic system containing the components in the proportions Ti/Mo = 3 remained active during electrolysis for more than 14 h.

Similar results were obtained in the amalgam reduction of nitrogen in the titanium(III)–molybdenum(III)–catechol (H_2.Cat) system in an aqueous medium.[47] Catechol forms stable complexes with titanium ions, which remain stable in aqueous media over a wide pH range (from 5 to 13) and which react reversibly at the electrode:

$$Ti(cat)_3^{3-} + e \rightleftharpoons Ti(cat)_3^{4-};\ E^0 = -1.4V.$$

Molybdenum ions also form soluble complexes with catechol, whose composition depends on the pH of the medium and the method of preparation.[48,49] The most active system in the fixation of nitrogen can be obtained by reducing the initial $Ti_2(SO_4)_3$ or Na_2MoO_4 solution with a gradual increase in the alkalinity of the latter from pH 3–4 to pH 7 during electrolysis as a result of the evolution of hydrogen. Under these conditions, the reduction reaction Mo(VI) + e → Mo(V) is accompanied by the dimerisation $2Mo(V) \rightarrow [Mo(V)]_2$ according to polarographic data. The dinuclear dimolybdenum(V) complexes of catechol are reduced irreversibly under the conditions of electrolysis at a controlled potential, forming apparently polynuclear molybdenum(III) complexes. The yield of hydrazine and ammonia in the titanium(III)–molybdenum(III)–catechol system passes through a maximum for the ratio Ti/Mo = 6. In the absence of titanium(III) as well as in all the systems enumerated, molybdenum(III) exhibited a very weak catalytic effect, which made it possible to obtain only traces of hydrazine and ammonia.

The possibility of the electrochemical reduction of nitrogen in aqueous media in the presence of molybdenum complexes was first noted by Zueva et al.[50] However, these data as well as data on the amalgam reduction of nitrogen in methanol solutions, catalysed by molybdenum carbonyl complexes,[51] were poorly reproducible, although the fact itself of the formation of hydrazine was not open to doubt. Reproducible results were achieved using molybdenum(III) complexes as the catalysts, obtained by reducing molybdenum(V) in alkaline methanol solutions in the presence of magnesium ions.[52] The electrochemical[53–55] and kinetic[53,56] study of this system showed that the composition of the species active with respect to nitrogen includes molybdenum(III) and magnesium and that the catalytic complex functions in a state corresponding to its adsorption on the surface, although the catalyst is fairly rapidly deactivated during the reaction. The only nitrogen reduction product was hydrazine.

These results served as a basis in the search for molybdenum(III) complexes capable of being strongly adsorbed on the amalgam surface as a result of the surface activity of the ligand. After numerous surfactants of various nature had been tested, it was possible to observe an appreciable and satisfactorily reproducible increase of the catalytic activity of molybdenum(III) in the presence of dipalmitoylphosphatidylcholine (DPPC).[57] A characteristic feature of the structure of the DPPC molecules, which belong to the class of phospholipids, is a combination of hydrophobic "tails" (palmitic acid residues) with a dipole "head", incorporating the negatively charged phosphate group and the positively charged quaternary ammonium group. Capacitance measurements have shown[58,59] that the DPPC molecules form an adsorption layer on the negatively charged surface of the mercury electrode, being arranged vertically with the "head" towards the surface and the hydrophobic "tails" towards the solution. It has been suggested[56] that the active species is a dinuclear dimolybdenum(III) complex stabilised as a result of interaction with the phosphate (or carbonyl) groups in the adsorbed DPPC. The identical activation energies (~36 kJ mol^{-1}) for the formation of N_2H_4 and NH_3 show that, in the parallel reactions in which these products are formed, there apparently exists a common rate-limiting stage. This stage may be electron transfer from the amalgam to the active complex with formation of a molybdenum derivative of hydrazine (N_2^{4-}). This process is facilitated by the synchronous transfer of protons from the solvent via the hydrophobic layer of DPPC and the formation of the fragment $N_2H_n^{(4-n)-}$. At nitrogen pressures in excess of 50 atm, when the rate of formation of N_2H_4 and NH_3 ceases to depend on pressure, the yield of products calculated relative to the sodium content in the amalgam is approximately 2%.

Further improvement of this catalytic system was achieved by introducing tertiary phosphines, in the presence of which an appreciable catalytic effect was observed already at atmospheric nitrogen pressure.[60] The cocatalytic effect of phosphines was attained only in the presence of a phospholipid; their joint (synergistic) action increased the rate of reaction by a factor of three compared with its rate in the absence of the phospholipid, so that it was virtually identical with the rate of biological fixation of nitrogen (0.1–1 of a N_2 molecule per second per active centre). At a nitrogen pressure of 50 atm, the N_2H_4 concentration reached 2.6×10^{-2} M and the yield relative to the sodium in the amalgam which reacted was 20%.

Recently the fixation of nitrogen in the molybdenum(III)–DPPC–phosphine catalytic system was achieved also under the conditions of electrolysis at a mercury cathode.[61] Although the structure of this multicomponent and most active of all the known nitrogen-fixing systems is still not clear in its details, its investigation by cyclic and a.c. voltamperometry[54,55,62] has to some extent thrown light on the functions of the individual components. Thus it has been suggested that in the adsorption layer there are two types of molybdenum(III) complexes, one of which, containing only molybdenum, binds and activates nitrogen (activator) but exchanges electrons with the electrode only slowly.[62] The second complex—a molybdenum–magnesium complex—does not activate nitrogen but exchanges electrons with the electrode and the activator rapidly and reversibly and thus can function as a redox transferring agent, which is essential for the coupling of the electrochemical and chemical stages of the catalytic process. As a result of the strong adsorption properties of the transferring agent, its concentration on the amalgam surface greatly exceeds the content of the activator. The phospholipid coordinated to the activator increases the degree of adsorption of the layer and approximately equalises the surface concentrations of both components, maintaining them in the proportions optimum for the effective functioning of the catalytic system. The incorporation of the activator in the lipid film specifies a fully defined spatial disposition of the active centre, relative to the electrode on amalgam surface, and, furthermore, it prevents the deactivation of the catalyst during the reaction of the kind observed in the system without a phospholipid.[53] Coordination to phosphines enhances the electron-accepting properties of the transferring agent (and possibly also the activator), which should increase the rate of electron transfer from the amalgam to the substrate. Overall, the creation of a sterically ordered activator–transferring agent–outer electron source (amalgam or electrode) system lowers the energy barrier to electron transfer to the coordinated nitrogen molecule, as a result of which a catalytic effect comparable to the rate of an enzyme process is achieved.

Among other metal complexes catalysing the electrochemical reduction of nitrogen in protic media (water, THF–CH_3OH mixture), mention may be made of the clusters $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$.[63] Electrolysis in the presence of these complexes at $E = -1.7$ V, atmospheric nitrogen pressure, and 20 °C leads to the formation of NH_3 in a current yield of 1.6%.

Mention may also be made of studies on the reduction of N_2 to NH_3 in aqueous hydrochloric acid solutions in the presence of molybdenum complexes and zinc chloride[64] and on the direct reduction of N_2 at an iron cathode in alkaline solutions[65] with a current yield of ammonia not exceeding 1%. The detection of small amounts of ammonia must be checked carefully by carrying out parallel experiments with an inert gas or $^{15}N_2$. Without such a check, there is a possibility of erroneous conclusions about the feasibility of the reduction of nitrogen in particular systems. How likely is the risk of such an error is demonstrated by a study[66] in which it was shown by means of a repeated test in an inert gas atmosphere that the NH_3 detected in the electrochemical and photoelectrochemical reduction of nitrogen at an iron semiconductor (GaP) cathode is formed as a result of the reduction of the admixtures of nitrates and nitrites in the reagents employed. The reduction of nitrogen reported in studies[64,65] where no such check was made is therefore open to doubt.

The main disadvantage of all the electrochemical systems for the reduction of molecular nitrogen known at the present time is the low current yield of ammonia and hydrazine. This is associated with the occurrence of the parallel hydrogen evolution reaction whose rate is significantly higher.

Overall, studies on the electrochemical reduction of nitrogen in protic media are of great theoretical interest and have laid the foundations for future technologies for the synthesis of NH_3 and N_2H_4 under mild conditions. However, it must be recognised that these studied have not so far gone beyond the framework of purely laboratory methods.

Systems incorporating a powerful chemical reductant (organomagnesium, organolithium, and organoaluminium compounds, lithium tetrahydroaluminate, and metallic magnesium) and a transition metal compound capable of forming a complex with molecular nitrogen, which were discovered by Vol'pin and Shur in 1964,[67] served as a basis for the development of a nitrogen reduction process in aprotic media. The final products of the reduction of nitrogen in these systems are compounds of the nitride type, whose hydrolysis can yield ammonia. In the presence of aprotic Lewis acids, the amount of bound nitrogen exceeds by a factor of tens and hundreds the amount of catalyst used.

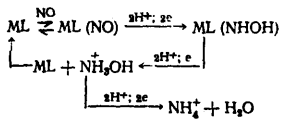
A series of electrocatalytic systems have been proposed,[68] the most effective of which makes it possible to obtain about 3 moles of ammonia per mole of a titanium compound when nitrogen is blown through a cell with an aluminium anode and a nichrome cathode filled with a solution of naphthalene and titanium and aluminium isopropoxides in dimethoxyethane. The reaction mechanism was not investigated, but it has been suggested that naphthalene fulfils the function of a redox transferring agent, aluminium isopropoxide plays the role of the Lewis acid, and the catalyst is the alkoxy-derivative of titanium(II).

A fundamentally new approach to the direct synthesis of organonitrogen compounds, especially aromatic amines,[67] from molecular nitrogen presupposes either the insertion of nitrogen in a metal–aryl bond or direct nucleophilic attack on the nitrogen ligand by a carbanion with subsequent reduction of the ArN=N group coordinated to the metal. Stable diazoalkane, diazenide, and hydrazide derivatives, from which free amines can be isolated by degradative methods, have been obtained by the direct alkylation and acylation of the nitrogen ligand.[69]

The degradative isolation of substituted hydrazines and amines from the hydrazido- and diazenido-complexes of molybdenum and tungsten can be replaced by the electrochemical reduction of these complexes at mercury or platinum cathodes in an aprotic medium using the traces of water in the solvent as the source of protons.[70,71] *N*-Aminopiperidine[70] and 5-amino-4-cyanopyrazole [71] were then obtained in 60–70% yields. Although this approach is very attractive, the problem of creating a continuous catalytic cycle for the synthesis of amines from molecular nitrogen is still far from being solved. The principal difficulties which must be overcome are associated with the appreciable contribution of side reactions and also with the difficulty of regenerating the initial complexes and isolating the target product from the reaction mixture without decomposing the catalytic system.

The interest in the problem of the electrocatalytic reduction of NO is associated with the attempt to utilise under mild conditions the nitrogen oxides contained in the waste gases from many chemical industries. In contrast to the known methods for the heterogeneous reduction of NO with H_2, CO, or NH_3 (see, for example, Seiyama et al.[72]), the electrochemical utilisation of NO does not require high pressures and temperatures. Successful attempts have been made both at the direct electrochemical reduction of NO and at its electrochemical reduction in the presence of metal complexes with formation of N_2O, N_2, NH_2OH, N_2H_4, and NH_3 as the products.[72,73]

In weakly acid aqueous solutions in the presence of transition metal (Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) complexes of ethylenediaminetetraacetate (EDTA), the electrochemical reduction of NO at the semiconducting GaAs electrode is accompanied by the selective formation of NH_3 (degree of conversion 22–31%) at room temperature and atmospheric pressure.[74] Similar results have been obtained at a platinum electrode ($E = -1.8$ V) using FeL_3^{2+} complexes (L = phen or bipy) as the catalyst; the degree of conversion of NO into NH_3 is 74–84%.[75] Finally, the selectivity of the conversion of NO into NH_3 at a carbon glass electrode modified with cobaltphthalocyanine reaches 92% (current yield 63%), while at a platinum electrode modified with poly(4-vinylpyridine)iron(II) (a redox catalyst), it does not exceed 2%.[76] This indicates that the reduction of NO proceeds via the coordination, rather than the redox-catalytic, mechanism. Presumably the coordination of NO to the metal is accompanied by a shift of electron density to the NO molecule, which activates it and results in its reduction. The mechanism for the reduction of NO to NH_3 catalysed by a metal complex (ML) can then be represented, for example, in the following manner:[75,77]



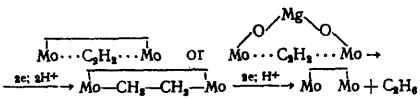
3. Reduction of Compounds with Triple Bonds

The reduction reactions of acetylene, the cyanide ion, nitriles, and isonitriles can be usefully removed to a separate chapter, since they are frequently regarded as model reactions for the reduction of molecular nitrogen, because these substrates are isoelectronic with nitrogen molecule and are in the main electrochemically inactive.

In the series of compounds with multiple bonds whose reduction is catalysed by molybdenum(III) complexes, acetylene is the most convenient substrate for the investigation of the kinetics and mechanism of the electrocatalytic reaction, since the hydrocarbons formed in it can be readily analysed by gas chromatography and the ratio of the products is extremely sensitive to the structure of the catalytically active species. The cysteine complexes of molybdenum(III) catalyse in aqueous solutions (pH 8–10) the electrochemical reduction of acetylene to ethylene and ethane in the proportions $C_2H_4 : C_2H_6 = 0.8$ and in these and other systems, which will be discussed below, ethylene is not reduced and thus ethane is formed from acetylene without the emergence of the ethylene derivative from the coordination sphere of the catalyst.[78,79]

Molybdenum(III) citrate complexes exhibit a similar catalytic activity.[80] It has been suggested[79,80] that a vacancy for the coordination of acetylene (C_2H_2) is liberated as a result of the dissociation of the oxo bridge bonds between the molybdenum(III) ions in the dimeric complex formed on reduction of the initial cysteine or citrate complexes of molybdenum(V). This conclusion agrees well with the fact that the stable complex Na_2MoO_4 (EDTA), in which such dissociation of the bonds after the reduction of molybdenum(VI) to molybdenum(III) does not occur, is catalytically inactive.[79] However, the replacement of the oxo bridges by the more labile sulphide bridges in $Na_2Mo_2O_3S$ (EDTA) or $Na_2Mo_2O_2S_2$ (EDTA) makes the dissociation of the bridge bonds again possible and catalytic activity appears. This entails an increase in selectivity with respect to ethane and the attainable product ratio $C_2H_4 : C_2H_6 = 0.2–0.3$ differs sharply from the ratio characteristic of the cysteine and citrate complexes.

When magnesium ions are introduced into the system containing molybdenum(III) citrate complexes, the current yield of the reaction products becomes quantitative and the selectivity with respect to ethane increases,[80] which suggests that the mutual approach of two molybdenum(III) ions as a result of the appearance of an elongated bridge, made up of a bidentate carboxylate ligand or the magnesium ion, creates a possibility for the linear coordination of C_2H_2 between the molybdenum ions, which is similar to the coordination of nitrogen examined above and favours a more far-reaching reduction of acetylene to ethane via the intermediate dimolybdenum derivative:



In the products of the amalgam reduction of C_2H_2 in the presence of molybdenum(III) and tungsten(III) citrate complexes, appreciable amounts of methane, propane, and propene were detected together with C_2H_4 and C_2H_6.[81,82] The formation of methane (CH_4) indicates an increase in the lifetime of the dimetallic ethane derivative M=CH–CH=M because of the weakening of the proton-donating properties of the medium, as a result of which its further reduction with cleavage of the carbon–carbon bond becomes possible.[81] It has been suggested that this cleavage is accompanied by the formation of carbenoid intermediates of the type $M=CH_2$, whose secondary reactions with C_2H_2 lead to the appearance of propane and propene in the reaction products.[82]

In all the electrocatalytic systems enumerated above, the rate of reaction depended exponentially on the cathode potential and thus the rate-limiting stage is electron transfer from the electroce to the catalytically active species containing a coordinated acetylene molecule. In contrast to this, in the system incorporating the catechol complexes of titanium(III) and molybdenum(III), the rate of reaction no longer depended on the cathode potential and was approximately an order of magnitude higher than in the system without titanium(III).[83] As in the amalgam reduction of nitrogen,[47] it has been suggested that $Ti(cat)_3^{3-}$ functions as the catalyst transferring electrons from the electrode to the catalytically active species in the bulk of the solution.

The iron-molybdenum cofactor isolated from nitrogenase has been used[84] as the catalyst for the electrochemical reduction of C_2H_2. The main product of electrolysis at a mercury cathode in the borate buffer (pH 9.6) at $E = -1.8$ V was C_2H_4 with a current yield of 2%. Nitrogenase also catalysed this reaction but only in the presence of adenosinetriphosphate and methylviologen as the catalytic transferring agent, since the direct electron transfer from the electrode to the active centre of the enzyme was prevented by its protein environment.

The stoichiometric reaction involving the reduction of C_2H_2 to C_2H_4 by a synthetic analogue of ferredoxin containing a cluster with the cubane structure, i.e.

$$2\,[Fe_4S_4(SR)_4]^{3-} + C_2H_2 + 2H^+ \rightarrow 2\,[Fe_4S_4(SR)_4]^{2-} + C_2H_4\ ,$$

where R = Ph or p-MeC_6H_4,[85] has been used to set up an electrocatalytic cycle in which the reduced form of the cluster was constantly regenerated at a mercury cathode:[86]

$$2\,[Fe_4S_4(SR)_4]^{2-} \overset{2e}{\rightleftharpoons} 2\,[Fe_4S_4(SR)_4]^{3-} \xrightarrow{C_2H_2;\ 2H^+} 2\,[Fe_4S_4(SR)_4]^{2-} + C_2H_4\ .$$

The conclusions concerning the role of iron sulphide and iron molybdenum sulphide clusters in the electrocatalytic reactions must be treated with caution, since the dissociation or decomposition of the cluster into low-molecular-weight fragments is possible in their reduction. In particular, in methanolic solutions of $FeCl_2$ (or $FeCl_3$) and Li_2S, sodium amalgam reduces C_2H_2 to C_2H_4 and C_2H_6 with an activity close to that of the cluster $[Fe_4S_4(SBu)_4]^{2-}$, which decomposes under the conditions of amalgam reduction.[87]

The modification of the surface of the electrode prepared from polymeric sulphur nitride $(SN)_x$ by molybdenum ions (possibly via their binding to the surface sulphur atoms) made it possible to obtain an electrode on which acetylene was selectively reduced to ethylene with a quantitative current yield and which exhibited an activity exceeding that of nitrogenase.[88]

Electrocatalytic systems based on molybdenum complexes have also been used to reduce other substrates with triple bonds. Thus, in the presence of molybdenum(III) citrate complexes at a mercury cathode at a potential of −1.8 V, the cyanide ion is reduced to NH_3 and CH_4; furthermore, C_2 and C_3 hydrocarbons are produced in smaller amounts.[89] In the reduction of CH_3CN in the same system, propane and propene were found together with the main products C_2H_6 and NH_3, which indicates the dissociation of the C–C bond in the activated CH_3CN molecule with the intermediate formation of, apparently, the carbenoid fragment $Mo{=}CH_2$ and the growth of the carbon chain in its interaction with the next CH_3CN molecules.[90] The formation of amines in these systems was not observed.

The iron sulphide and iron molybdenum sulphide clusters already mentioned catalyse the reduction, in a protic medium, of methyl isonitrile to CH_4, C_2H_4, and C_2H_6 and of acetonitrile to C_2H_6 and NH_3.[91] Under the same conditions, the azide ion is reduced to N_2H_4, NH_3, and N_2,[92] while N_2H_4, NH_3, and RNH_2 are formed from RN_3 (R = CH_3 or HOC_2H_4).[93] The reduction can be carried out, in particular, in an aqueous borate buffer solution (pH 10) at a chemically modified electrode prepared by depositing the $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ cluster from solution in acetonitrile onto the surface of an electrically conducting support. However, the activity of this electrode decreases with time as a consequence of the deposition of the cluster from the electrode surface.[93]

4. Reduction of Carbon Oxides

The creation of catalysts for the low-temperature reduction of carbon monoxide and dioxide is of potentially very great importance, since, as the coal, petroleum, and natural gas resources are exhausted, carbon monoxide may becomes a source of raw material for the synthesis of various organic compounds.

A review has been devoted[94] to questions of the coordination chemistry of CO_2 and its biological, chemical, photochemical, and electrochemical activation. The amalgam or electrochemical reduction of CO_2 in the absence of metal complexes can lead to various products of the type of formate,[95] oxalate,[95,96] and many other organic compounds (tartrate, glycolate, etc.),[94] depending on the conditions (the material of the electrode, solvent, etc.).

The purely electrochemical reduction of CO_2 is an energy consuming process, since the formation of the radical-anion $CO_2^{\cdot-}$, which is the primary product of the conversion of CO_2, takes place at potentials of approximately −2 V.[94] The situation may change significantly when metal complex catalysts are used. The possibility of involving CO_2 in the electrolytic carboxylation of organic halides was already mentioned previously.[17] Another reaction catalysed by metal complexes is the reduction of CO_2 to CO. The tetra-azamacrocyclic complexes of cobalt[97] and nickel,[98] $Re(bipy)(CO)_3Cl$,[99] $[Ru(bipy)_2.(CO)_2]^{2+}$,[100] RhL_2Cl (where L = diphosphines),[101] etc. serve as catalysts. The reaction is carried out in aqueous organic or aqueous media at atmospheric or elevated CO_2 pressures at different electrodes (mercury, carbon glass, platinum, etc.). The reduction prduct is the CO + H_2 mixture and under optimum conditions the current yield of CO reached 90–100%. In an alkaline medium, formate is formed together with CO.[100]

The electrolysis is carried out at the electrochemical reduction potentials of the metal complexes. In all cases, these potentials are more cathodic than the thermodynamic potentials of the reduction of CO_2 to CO.[94] The metal complexes retain their catalytic activity for a long time.[98–101] It has been suggested[99] that they play the role of redox catalysts in this reaction. However, it may be thought that, since this reaction is in fact the reverse of the metal complex-catalysed conversion reaction of water gas (CO + H_2O),[102] the function of the catalyst consists not only in electron transfer from the electrode to the CO_2 molecule but also in preliminary coordination and activation of the latter. The absence of formate from the products indicates, according to the authors,[99] that hydride derivatives capable of reducing CO_2 to formate are not formed in the reduction of the metal complexes.

The complex $Rh(bipy)_2^+$, electrogenerated from $[Rh(bipy)_2.(CF_3SO_3)]^{2+}$ in acetonitrile at the potentials of the $Rh(bipy)_2^{0/-}$ redox transition (E^0 = −1.55 V), reduces CO_2 catalytically at atmospheric pressure to formate with a current yield of 64%.[103] The formation of the product is described by a stoichiometric scheme with participation of the cations of the supporting electrolyte Bu_4N^+:

$$Bu_4N^+ + CO_2 \overset{2e}{\rightarrow} HCO_2^- + Bu_3N + CH_2{=}CHEt\ .$$

It was shown in the same study that the complex $Ru(trpy).(dppe)$ [where trpy = 2,6-di(2-pyridyl)pyridine], electrogenerated by the irreversible two-electron reduction of $Ru(trpy)(dppe)Cl^+$, catalyses, under analogous conditions at E = −1.4 V, the reduction of CO_2 in accordance with the stoichiometric scheme

$$Bu_4N^+ + 2CO_2 \overset{2e}{\rightarrow} Bu_3N + CH_2{=}CHEt + CO + HCO_3^-\ .$$

It is suggested that the catalytic activity of metal polypyridyl complexes is due to the possibility of their electrochemical reduction accompanied by the ejection of the $CF_3SO_3^-$ or Cl^- anions and the appearance in the coordination sphere of a free site for the binding of CO_2. The subsequent reduction of CO_2 in the coordination sphere leads to products whose nature depends significantly on the basicity of the intermediates in the reduction of CO_2. The polypyridyl ligands, which play the role of a kind of "electron reservoir", apparently have an important function in the catalytic activity of these complexes.[103]

The cluster $[Fe_4S_4(SR)_4]^{2-}$ (where R = Ph or $PhCH_2$), which has the cubane structure and is a model of ferredoxin, catalyses in DMF at $E = -1.7$–2.0 V the electrochemical reduction of CO_2 on mercury with formation of formate, oxalate, and carbon monoxide as the products.[104] The same products are formed also in the non-catalytic electrochemical reduction of CO_2 but at much more cathodic potentials (−2.4 V). Furthermore, whereas the non-catalytic reduction of CO_2 leads mainly to the oxalate, the principal product in the catalytic process is formate (selectivity up to 93%). By varying the composition of the electrolyte, it is possible to drive the process towards the required product.

Thus the use of transition metal compounds capable of forming complexes with CO_2 can ensure the operation of a particular catalytic reduction mechanism. The reduction of CO_2 to formaldehyde, methanol, and hydrocarbons is more promising. For a number of reasons, it is desirable to carry out the reaction in protic media. Only the first steps have been taken along these lines. Thus it has been shown[105] that reduction of CO_2 with zinc amalgam catalysed by VO^{2+} ions in acid aqueous solutions (pH 2.5) leads to the formation of formaldehyde, methanol, and methane together with formic acid. In the presence of titanium ions, aluminium amalgam reduces CO_2 selectively to CH_2O alone under the usual conditions.[106] The reaction proceeds within a narrow pH range in the vicinity of 3.5, which enabled the authors[106] to put forward the hypothesis that the catalytically active species is formed by the association of two titanium ions.

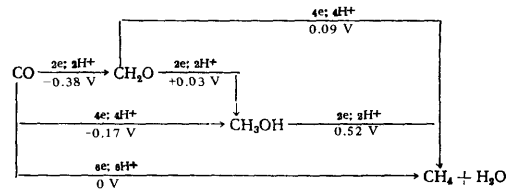
The molybdenum(III) complex of catechol catalyses the electrochemical reduction of CO_2 at a mercury cathode to C_1–C_3 hydrocarbons.[107] The reduction was carried out in an aqueous buffer solution (pH 7) under the conditions of galvanostatic electrolysis (i = 7 mA cm^{-2}). The reaction is accompanied by the vigorous evolution of hydrogen and the overall yield of hydrocarbons does not exceed 0.2%. It is of interest that the formation of oxygen-containing products of the reduction of carbon dioxide (CO, CH_2O, HCO_2H, and CH_3OH) was not observed and the rate of reaction increased by a factor of 5 after the introduction into the system of $Ti(cat)_3^{3-}$, which is itself inactive in relation to CO_2. It has been suggested that CO_2 is reduced in the coordination sphere of Mo(III) via a mechanism involving inner sphere catalysis without the emergence of intermediates into the bulk of the system. This system is of interest also because outer sphere redox catalysis takes place in it together with the inner-sphere catalysis, since $Ti(cat)_3^{3-}$ fulfils the function of an agent transferring electrons from the cathode,[47,83] The formation of C_1–C_3 hydrocarbons was observed also in the reduction of CO_2 catalysed by $[Fe_4S_4(SR)_4]^{2-}$.[104]

Other classes of transition metal complexes catalysing the electrochemical reduction of CO_2 are metallophthalocyanines and metalloporphyrins. This question has been considered in greatest detail by Tarasevich and Radyushkina.[3] The main reduction products are oxalic and gluconic acids. One may also mention a study[108] in which it was shown that $VO(acac)_2$ in acetonitrile catalyses the electrochemical reduction of CO_2 at the potentials at which the corresponding vanadium(II) complex is generated, but the reduction products were not identified.

Thus the possibility of the formation of complexes of CO_2 with transition metal compounds and the possibility of the inner sphere electron transfer to the coordinated CO_2 molecule at much more anodic potentials than in the purely electrochemical reduction demonstrate that MCE is promising in various carbon dioxide conversion reactions.

The involvement of carbon monoxide in catalytic reactions leading to the synthesis of organic compounds has long formed an industrial application. It is sufficient to point out the processes involving the formation of synthol via the Fischer–Tropsch reaction, the carbonylation of methanol with formation of acetic acid, the conversion of water gas, etc.[2] On the other hand, the reactions involving the electrochemical conversion of CO began to be investigated comparatively recently. This is because the electrochemical reduction of carbon monoxide takes place at extremely negative potentials, since the thermodynamics of this process are apparently determined primarily by the potential corresponding to the reduction of CO to the radical-anion $CO^{\cdot-}$. Thus CO can be reduced chemically only with the Na–K alloy in THF.[109] After the hydrolysis of the reaction mixture, the glycolate and oxalate anions as well as $C_3O_3^{2-}$ are then formed as the final products. The electrochemical reduction of CO at pressures of several hundreds of atmospheres at a steel cathode under the conditions of galvanostatic electrolysis leads to the formation of squaric acid $C_4O_4H_2$.[110] Apparently, in liquid ammonia (−50 °C), in the presence of 0.1 M KI, carbon monoxide is reduced at various cathodes at potentials close to the potentials at which the solvated electron (e_S^-) is generated.[111] However, the attempt at a preparative electrochemical reduction of CO under these conditions failed. Only the reduction of CO by electrogenerated e_S^- leads to the formation of the dimeric anions $C_2O_2^{2-}$, which are precipitated as a deposit of the salt $K_2C_2O_2$.

The use of many-electron reactions should significantly improve the energetics of the reduction of carbon monoxide. The thermodynamics of the reduction of CO to the simplest organic compounds confirms this.

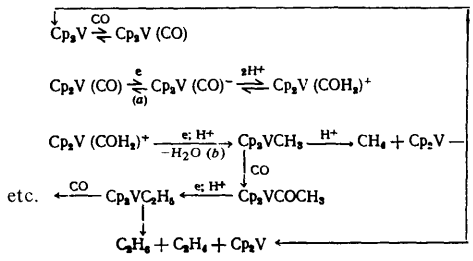


Despite the favourable thermodynamics, the direct amalgam or electrochemical reduction of CO at a mercury cathode is impossible, apparently because of kinetic limitations. The picture changes significantly when CO is coordinated to transition metal complexes, i.e. under the conditions of coordination electrocatalysis, where the catalyst–substrate complex with an activated CO molecule is reduced.

The fruitfulness of this approach was first demonstrated in relation to the vanadocene-catalysed amalgam reduction of CO with formation of C_1–C_4 hydrocarbons.[112–116] It was shown[112,113] that Cp_2V effectively catalyses the reduction of CO with sodium amalgam even at room temperature and atmospheric CO pressure in aprotic solvents (DMF, THF, etc.) containing diethylbarbituric acid or a phenol as the proton donor. The main product is methane (85–95%) and the remainder consists mainly of saturated C_2–C_4 hydrocarbons. Under optimum conditions, more than 100 molecules of hydrocarbons are formed per catalyst molecule and the periodic introduction of consumable reagents into the system (amalgam, CO, and a proton donor) makes it possible to achieve a continuous process.[112] This reaction is a kind of electrochemical analogue of the Fischer–Tropsch synthesis, proceeding with participation of the adsorbed catalyst and being characterised by the transfer of the first electron to the coordinated substrate molecule in the direction opposite to that of the standard potential drop, since $E^0[Cp_2V(CO)^{0/-}] = 2.3$ V and the amalgam potential is approximately −2.1 V.[114] We may note that this is the first case of endoergic electron transfer[6]

in MCE, known to us, which has been demonstrated experimentally. Vanadocene also catalyses the evolution of oxygen, as a result of which the current yield of hydrocarbons does not exceed 10%.[114]

Both reactions (the reduction of CO and the evolution of H_2) take place in the adsorption layer without the emergence of the intermediate reduction products into the bulk of the solution and their kinetics is described taking into account the surface and not the bulk-phase concentration of the catalyst. Carbon monoxide is reduced at potentials which are insufficient for the intermediate formation of the hydride Cp_2VH^-, which makes it possible to rule out the hydride mechanism of the reduction of CO and explains the absence of CH_2O and CH_3OH from the reaction products.[113,114] Finally, the formation of C_2–C_4 hydrocarbons and also the growth of the hydrocarbon chain in the Fischer–Tropsch synthesis take place as a result of the insertion of CO in the metal–alkyl bond in the intermediate alkyl complexes Cp_2V–Alk,[115] which yet again indicates the retention of the general characteristics of MCC in electrocatalysis. The catalytic cycle of the vanadocene-catalysed electrochemical reduction of CO can be represented schematically as follows:[115,116]



Stage (*a*) is endoergic and occurs because of the presence in the cycle of the rapid and irreversible stage (*b*) in which the C–O bond is ruptured.

The efficiency of metal complex electrocatalytic systems depends significantly on the stability of the catalyst. Thus, together with vanadocene, other electrochemically generated metallocenes of Group VB and VIB metals likewise catalyse the electrochemical reduction of CO in aprotic solvents containing proton donors, but the catalytic activity of systems based on them decreases to zero fairly rapidly.[117] This is due to the metastability of the complexes Cp_2M (M = Nb, Mo, or W) responsible for the coordination of CO.

The advantage of electrocatalytic reactions in theoretical research consists in the possibility of using electrochemical methods for their investigation. For the electrochemical reduction of CO catalysed by metallocene dichlorides, it has been possible not only to identify by electrochemical methods the primary products of the interaction of the catalyst with CO and to reach a conclusion about the nature of the catalytic activity of the species, but also to elucidate the cause of the differences between the catalytic activities of the complexes Cp_2MCl (M = Ti, V, Nb, Mo, or W), which consists in the different stabilities of the metallocenes or their cations responsible for the coordination of CO, and also to characterise the kinetic thermodynamic regions where these are stable.[117,118] The thermodynamics of the region corresponding to the stability of catalysts is an important factor which must be taken into account in the development of metal complex electrochemical systems. Without taking it into account, one can over-reduce or, conversely, oxidise the catalyst, which would alter the electronic configuration of its constituent metal, making it unfavourable for the coordination of the substrate, so that the catalyst loses its activity. The studies where the possibility of predicting the thermodynamic stability of neutral and ionic metal complexes on the basis of tabulated ionisation potentials of the corresponding metals has been demonstrated in relation to sandwich and wedge-sandwich metal complexes, catalytically active in numerous reactions,[67,122] merit attention in this connection.[119–121]

The electrochemical reduction of CO to C_1–C_3 hydrocarbons can be achieved also in aqueous solution ($6 < pH < 13$) using the catechol complex of molybdenum(III) adsorbed on the mercury cathode as the catalyst.[123] As in non-aqueous media, the main product is methane (80–90%) and the overall current yield of hydrocarbons is a fraction per cent, since the main bulk of the electricity is consumed in the parallel H_2 evolution reaction catalysed by the same molybdenum(III) complexes. The efficiency of this system increases appreciably after the introduction of $Ti(cat)_3^{3-}$, which is manifested by an increase in the rate of reaction and in the current yield of the hydrocarbons to 15%.[124] The kinetic and electrochemical studies of this system have led to the conclusion that the catalytic species in relation to CO is a carbonyl complex of molybdenum(III) and the reversible $Ti(cat)_3^{2-/3-}$ pair functions as a redox catalyst. Thus, when a redox catalyst is introduced into the system, electron transfer also to molybdenum(III) complexes, activating the CO molecule but having no direct contact with the electrode, becomes possible as a result of which the overall rate of reaction increases. This is an excellent example of the combination of coordination catalysis [activation and inner-sphere reduction of CO in the presence of the molybdenum(III) complex] and redox catalysis [electron transfer by the $Ti(cat)_3^{3-}$ complex to the molybdenum(III) carbonyl complex] which leads to an increase in the catalytic efficiency of the system.

The electrocatalytic reduction of CO by metal complexes can yield not only hydrocarbons but also oxygen-containing products. At room temperature and atmospheric pressure, CO is reduced selectively in aqueous solutions (pH 3.5) to methanol at a platinum electrode modified by the complex $[Fe^{II}(CN)_6]Fe^{II}K_2$ (A) at $E = -0.9$ V.[125–127] Methanol is also formed at a non-polarised cathode, the process being accompanied by the oxidation of the complex (A) to $Fe^{II}(CN)_6 . Fe^{III}K$ (B). It has been suggested that the CO molecule is activated as a result of its incorporation into the coordination sphere of the anion $[Fe(CN)_6^{4-}]$ with displacement of CN^- and the formation of $[Fe(CN)_5(CO)]^{3-}$ and the subsequent reduction of CO in MeOH via a redox catalytic mechanism [the catalyst is the (A)/(B) redox pair].[125,126]

There are relatively few data on the electrochemical oxidation of CO catalysed by metal complexes. One can only mention a study[128] where it was shown that in aqueous solutions of HX (X = Cl, Br, or I) the complex $[Rh(CO)_2X_2]^-$ catalyses the oxidation of CO to CO_2 on carbon glass at potentials of approximately 0.4 V. This reaction is thought to be promising for use in fuel cells.

5. Oxidation of Water and Organic Compounds

The oxidation of water to oxygen is a complex many-electron process, which gives rise to certain requirements to be met by the metal complex catalyst of this reaction, which are extremely similar to the requirements imposed on the catalysts of the reduction of nitrogen: it is necessary that the metal complex should be able to "switch over" the reaction from the thermodynamically unfavourable one-electron mechanism to the more favourable many-electron mechanism.[129–131] Only then do the thermodynamics of the overall oxygen formation reaction become sufficiently favourable. By analogy with natural photosynthesis, it has been suggested[129]

that the metal complex should consist of a dinuclear or tetranuclear cluster, each atom of which is capable of accepting respectively two electrons or one electron, such acceptance being reversible since only then is it possible to achieve an efficient operation of the catalyst. Polynuclear complexes can also be used, but in this case the oxidation of water would proceed via the intermediate formation of a peroxy-derivative. However, this would happen only if the metal atom in the complex is capable of changing its valence by two units.

The use of such approaches[132,133] showed that simple hydroxo-complexes of iron(II) and cobalt(II) are effective catalysts of the electrochemical oxidation of water. This is due to the ability of these metals to change their valence by two units with formation of highly reactive M(IV) complexes, oxidising water to the peroxide, which is rapidly oxidised further under these conditions or decomposes catalytically at the electrode, affording oxygen. The mechanism of the electrocatalytic oxidation of water with participation of hydroxo-complexes of iron and cobalt (MOH^+) can be represented by the scheme[132,133]

$$M^{II}OH^+ \xrightleftharpoons{2OH^-} M^{II}(OH)_3^- \xrightarrow{-2e} M^{IV}(OH)_3^- \rightarrow M^{II}OH^+ + H_2O_2 \quad . \qquad (1)$$

The catalytic process is apparently of a mixed bulk-phase–surface character although the appearance of a catalytic oxidation wave on the voltage–current plots even at Fe^{2+} and Co^{2+} concentration in the range 10^{-8}–10^{-6} M indicates a significant contribution of the bulk-phase process.[132]

The development of catalysts for the oxidation of water is important also from the standpoint of the solution of the problem of its photocatalytic oxidation. In particular, using iron and cobalt hydroxo-complexes, some of the first catalytic systems for the oxidation of water with high quantum yields under the influence of visible light have been developed.[134,135] Detailed kinetic study led to the conclusion[136–139] that the mechanism of the catalytic action of the hydroxo-complexes in the reactions involving the oxidation of water by one-electron oxidants is more complex than the one represented by the overall Eqn.(1).

In subsequent studies, whose authors attempted to use the complexes of the same transition metals but with other ligands are homogeneous catalysts of the electrochemical and chemical oxidation of water, the high activity of even traces of the hydroxo-complexes led, in our view, to an erroneous interpretation of the data obtained. Thus it has been concluded[140] that the hypothetical complex $[Fe(bipy)_2(bipyH)(OH)]^+$ is a catalyst of the electrochemical oxidation of water. However, here no account was taken of the fact that in alkaline media the initial complex $Fe(bipy)_3^{2+}$ hydrolyses with formation of amounts of $FeOH^+$ which are quite sufficient for the appearance of a catalytic effect.[132] An analogous error was most probably made also by Zamaraev and Parmon[141] and Nord et al.[142] in studies of the chemical oxidation of water by one-electron oxidants. The solutions of iron and cobalt complexes with various ligands which they used as "catalysts" almost always contain traces of the corresponding hydroxo-complexes or hydrolyse with their formation. It has been shown[143,144] that such trace amounts are entirely sufficient for the observed catalytic effect.[141,142]

It has been reported[145,146] that the dinuclear complex $[(bipy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bipy)_2]^{4+}$ (C) oxidises water to oxygen during its electrochemical four-electron oxidation to $[(bipy)_2(O)Ru^{V}ORu^{V}(O)(bipy)_2]^{4+}$ in an acid medium. However, the authors note that the initial complex is destroyed during the catalytic reaction. It is entirely possible that the complex $RuO_2.xH_2O$, which is known to catalyse effectively the chemical and electrochemical oxidation of water to oxygen in an acid medium,[147] is formed in the course of the degradation. Furthermore, the complex (C) catalyses the chemical or electrochemical reactions in which Cl^- is oxidised to Cl_2.[148,149] In particular, this has been the cause of the erroneous conclusion[145] that the dimer (C) is catalytically active in the electrochemical oxidation of water, since traces of Cl^- ions were present in the electrolyte solution.

Thus, despite certain advances associated with the detection of the catalytic activity of the hydroxo-complexes or iron(II) and cobalt(II),[132,133] the problem of the development of metal complex catalysts for the electrochemical oxidation of water is still far from being solved.

Organic compounds can be oxidised with participation of a number of transition metal ions in the highest oxidation states (Co^{3+}, Ce^{4+}, MnO_4^-, Mn^{3+}, $Cr_2O_7^{2-}$, Tl^{3+}). Some of these reactions can be used to set up an electrocatalytic cycle in which the transition metal ion is regenerated in the initial state by oxidation at the anode. It is by no means always convenient to regenerate the oxidant in the presence of the substrate and this operation is frequently performed in a separate electrolyser and the substrate is then oxidised in another reactor. Analysis of the reactions using electrochemically generated oxidants is outside the framework of the present review. The necessary information about this question can be secured from a monograph[150] and another review.[151] We shall deal only with two examples of the use of metal complexes in oxidation reactions. One of them refers to the application of polypyridyl complexes of ruthenium(IV) as the catalytic transferring agents in the oxidation of organic compounds (S) [152] in accordance with the mechanism

$$[(trpy)(bipy)RuO]^{2+} + S + H_2O \rightarrow [(trpy)(bipy)RuOH_2]^{2+} + S{=}O$$
$$\uparrow \qquad\qquad -2e;\ -(E = 0.6\text{–}0.8\ V) \qquad\qquad \downarrow$$

The oxidation is carried out in a diaphragm electrolyser at a carbon glass anode in phosphate (pH 7) or borate (pH 9) buffer solutions at a metal complex concentration of about 10^{-3} M. Under these conditions, it is possible to oxidise 2-propanol to acetone, toluene to benzoic acid, *p*-xylene to terephthalic acid, and cyclohexene to *p*-benzoquinone via the intermediate formation of 2-cyclohexanone. The oxidation can be carried out using not only a dissolved metal complex but also one which was immobilised beforehand on the anode surface.[153]

The second example refers to the cathodic reactions in which oxygen is activated with participation of metal complexes or transition metal ions. Such activation can be achieved by reducing oxygen to hydrogen peroxide and regenerating from the latter the $OH^{\cdot}$ radical via the reaction of H_2O_2 with Fe^{2+} ions (Fenton's reagent). Electrocatalytic systems for the oxidation of polymethylbenzenes to the corresponding aldehydes[154] and also of aliphatic C_5–C_{30} hydrocarbons and 3-methylpentane to ketones[155] have been constructed in accordance with this principle. The electrolysis is carried out in hydrochloric acid solutions at a mercury cathode, the solution being saturated with oxygen. The following mechanism of the catalytic cycle has been proposed:[154]

$$\left.\begin{array}{l} Fe^{3+} \xrightarrow{e} Fe^{2+} \\ O_2 \xrightarrow{2e;\ 2H^+} H_2O_2 \end{array}\right\} \rightarrow Fe^{3+} + OH^{\cdot} \xrightarrow[-H_2O]{PhCH_3} PhCH_2^{\cdot} \xrightarrow{O_2}$$
$$\rightarrow PhCH_2OO^{\cdot} \rightarrow PhCHOOH \xrightarrow[-Fe^{3+};\ -OH^{\cdot}]{Fe^{2+}} PhCHO \quad .$$

The electrochemical activation of oxygen in hydrocarbon oxidation reactions has been achieved also via electron transfer to an iron–porphyrin complex deposited on the surface of a graphite electrode.[156] The electrode was impregnated with a benzene solution of iron-tetraphenylporphyrin chloride and

dried *in vacuo*. Hexane and 1,2-dimethylcyclohexane were oxidised to the corresponding hexanols under the conditions of potentiostatic electrolysis at $E = -1.5$ V in acetonitrile containing 10% of the hydrocarbon and 5×10^{-2} M acetic anhydride. The current yield of the alcohol was 7%. During the electrolysis, the system lost its activity and after 2 h the reaction ceased completely because the iron-porphyrin was completely washed off the cathode. It has been suggested that the oxidation of hydrocarbons (RH) at this electrode is described by the following consecutive reaction scheme (Pr = porphyrin):

$$\begin{array}{c} \mathrm{PrFe^{III} \xrightarrow{e} PrFe^{II} \xrightarrow{e} PrFe^{I}} \\ \downarrow O_2 \qquad \downarrow O_2 \\ \mathrm{PrFe^{III}O_2^- \xrightarrow{e} PrFe^{III}O_2^{2-} \xrightarrow[-AcO^-]{Ac_2O} PrFe^{III}OOAc \xrightarrow{-AcO^-}} \\ \rightarrow [\mathrm{PrFe^{IV}=O}]^+ \xrightarrow{KH} \mathrm{PrFe^{III}} + \mathrm{ROH}. \end{array}$$

The oxo-complex $[PrFe^{IV}=O]^+$ serves as the hydrocarbon oxidising agent. Overall, the catalytic cycle can be regarded as an electrochemical model of cytochrome P-450.

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Thus the use of metal complexes in the catalysis of electrode processes make it possible to reduce the energy consumption and to ensure the occurrence of electrochemical reactions of substrates which are electrochemically inactive or are discharged at electrodes with a high overpotential. The metal complex-catalysed reductive dehalogenation reactions are promising for practical applications, in particular, for the decontamination of waste water containing toxic organic halides and for the solution of certain problems in fine organic synthesis, including the synthesis of carboxylic acids from alkyl and aryl halides and carbon dioxide. The successful development of catalysts for the electrochemical oxidation of nitrogen and carbon monoxide, which make it possible to reduce these substrates at low cathodic potentials and to increase thereby the current yield of the products, enables us to count on fundamentally new possibilities in the electrosynthesis of hydrazine from N_2 and of organic compounds from CO (i.e. a raw material which is non-traditional for electrochemistry) at low pressures and temperatures. The use of metal complexes for the catalysis of electroprocesses in photoelectrochemical solar energy converters (catalysts of the oxidation of water) and current sources (catalysts of the reduction of CO and CO_2 and also of the oxidation of alkanes and CO) is also promising, although one must admit that the development of catalysts for these processes has not as yet gone beyond the framework of laboratory research.

The results presented in this review demonstrate only a small fraction of the possibilities which have arisen in metal complex electrocatalysis with a skilful combination of the principles of electrochemistry and homogeneous and heterogeneous catalysis with ideas derived from modern inorganic and organometallic chemistry. One may hope that the development of this undoubtedly promising field will lead to the discovery of many fundamentally new catalytic reactions and may possibly serve for the creation of new industrial processes.

During the preparation of the present review, there has been a sharp growth of the number of studies on the electrocatalytic reduction of CO_2 to CO. The complexes $\{Pd[PhP.(CH_2CH_2PPh_2)_2]R_3P\}^{2+}$ (where R = MeO, Et, Ph, or CH_2OH),[157] $Ni(bipy)_3^{2+}$, $Ni(dppe)_3^{2+}$,[158] $Re(CO)_3LCl$ (where L = bipy and its substituted derivatives),[159–162] $Ni(teta)^+$, and Co(salen) [163] have been used as catalysts in acetonitrile in the presence of various proton donors. Significantly more attention has been devoted in these studies to the electroanalytical investigation of the mechanism of the catalytic action of the metal complexes. In particular, it has been shown[157] that the key stage in the electrocatalytic cycle is the insertion of CO_2 in the Pd–H bond of the hydride complex formed as an intermediate in the electrochemical reduction. It has been noted[159,161,162] that the efficiency of the catalytic action and the stability of the complexes fixed on electrode-supports by electropolymerisation methods, by incorporation in a polymer matrix, etc. is significantly enhanced. The electrodes modified with an insoluble $K_2Fe[Fe(CN)_6]$ film catalyse the reduction of CO_2 and CO to methanol in an aqueous medium in the presence of water-soluble iron, nickel, cobalt, and chromium complexes.[164,165] The complex $Ru(bipy)_2.(CO)_2^{2+}$ catalyses the selective reduction of CO_2 to $HCOO^-$ in acetonitrile in the presence of $Me_2H_2N^+$ or PhOH as proton donors.[166] Individual examples of the catalysis of CO_2 reduction reactions and also of the dehalogenation of RX by phosphine, polypyridyl, and macrocyclic nickel complexes may be found in Troupel's paper.[167]

The possibility, in principle, of reducing nitrogen by protonating the complex $[W(N_2)_2(dppe)_2]$ with toluene-*p*-sulphonic acid in THF with subsequent electrochemical reduction of the resulting hydrazido-cation $[W(NNH_2)(p\text{-}MeC_6H_4SO_3).(dppe)]^+$ in an atmosphere of N_2 with formation of NH_3 and the regeneration of the initial dinitrogen complex has been demonstrated.[168,169] The products of the reduction of Cp_2TiCl_2 in THF and methanol catalyse the electrochemical reduction of N_2 to NH_3.[170] The current yield of ammonia does not exceed 1.5% and the results have not been confirmed by blank experiments (in an argon atmosphere) in experiments using $^{15}N_2$.

In an aqueous medium, macrocyclic cobalt and nickel complexes catalyse the electrochemical reduction of NO_3^- to hydroxylamine,[171] while water-soluble iron porphyrinates catalyse the reduction of NO_2^- to N_2O, NH_3, and NH_2OH;[172,173] the nitrosyl complex [Fe(NO)Pr] has been proposed to an intermediate in the last reaction.[173] A review[174] has been devoted to the consideration of the electrochemical oxidation reactions of organic compounds, H_2O, Cl^- and the reduction of NO_2^- catalysed by polypyridyl complexes of ruthenium and osmium. Other reviews[175–177] deal with studies in which metal complexes are used as redox transferring agents.

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The Oxidation-reduction Stage in the Nitration Reaction

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The mechanism of the nitration of aromatic compounds in which the initial stage is the oxidation of the aromatic substrate to the radical-cation is examined. Certain general preconditions, which make such a mechanism feasible, and also the available experimental evidence for its operation are analysed.
The bibliography includes 219 references.

CONTENTS

I. Introduction 144
II. The formation of the radical-cations of aromatic compounds under nitration conditions and their conversion into nitro-compounds 144
III. Nitration of aromatic compounds by the nitronium cation 148
IV. Catalytic nitration 150
V. The change in the mode of reaction after a change in the reactant ratio 153
VI. Nitration of aromatic compounds by tetranitromethane and metal nitrates 154
VII. The radical-ion mechanism of the nitramine rearrangement and the isomerisation of nitroarenium cations 155

I. INTRODUCTION

The reactions of organic compounds with electrophiles are known to begin with electron transfer from the substrate to the reactant and the formation of radical-cation (RC) of the organic compound:[1,2]

$$RH + E^{\cdot} \rightarrow RH^{+} + E^{-} \rightarrow \text{products}.$$

The oxidation-reduction stage in reactions of this type is frequently masked by the rapid subsequent reactions of the RC and the electrophile reduction product, which is a manifestation of the non-radical character of the overall process.[1,2] In such cases, the study of the reaction mechanism involves considerable experimental difficulties and its determination makes it necessary to resort to various indirect data apart from the investigation of the kinetics. These difficulties are a consequence of fundamental limitations characteristic of classical kinetics which make it impossible to obtain direct information about the fastest stages of chemical reactions. As a result, in the words of Hoffmann,[3] with the aid of kinetic studies it is possible to obtain "only the lower limit... to the number of stages in a reaction sequence and hence to the number of intermediate species".

The question of electron transfer as a possible elementary step in the reaction arises, in particular, in the study of the nitration of aromatic compounds. The energies of the highest occupied molecular orbitals (HOMO) of aromatic compounds are frequently close to or even exceed the energies of the lowest unoccupied molecular orbitals (LUMO) of the electrophiles involved in the nitration, which creates a possibility for an exoergic one-electron transfer in the direction from ArH to the electrophile in the case of activated aromatic substrates.

The experimental study of this problem, first formulated in the 1940's–1950's,[4-7] became possible only recently as a result of the advances achieved in the study of the RC of aromatic compounds ArH^{+}. Although the data obtained hitherto do not provide an exhaustive answer to the question of the role of the RC in nitration reactions, they nevertheless permit the conclusion that significant progress has been achieved in the solution of this problem. Some of these data are difficult to explain from the standpoint of classical ideas about the nitration mechanism[8] and are therefore of fundamental importance.

It is noteworthy that the problem of electron transfer as a possible stage in electrophilic substitution in aromatic compounds has already been frequently discussed.[9-16] However, it has not been the subject of a special detailed examination in relation to nitration. This factor and also the significant progress in the study of electron transfer processes in ArH–nitrating agent systems, which has occurred in recent years, made it desirable to write the present review devoted to the role of RC in nitration reactions.

II. THE FORMATION OF THE RADICAL-CATIONS OF AROMATIC COMPOUNDS UNDER NITRATION CONDITIONS AND THEIR CONVERSION INTO NITRO-COMPOUNDS

1. One-Electron Oxidation of Aromatic Compounds By Nitrating Agents

The oxidation reactions of aromatic compounds under the influence of nitrating agents are extremely varied and have long been known.[17] However, the possibility of the simplest of them, namely the one-electron oxidation of aromatic substrates in which the latter lose one π electron and are converted into highly active RC, has been demonstrated only recently:

$$ArH \xrightarrow[-e]{\text{nitrating agent}} ArH^{+}$$

The range of ArH capable of reacting in this way is fairly wide and according to the available data includes aromatic compounds with strong and moderate reducing properties, such as naphthalene,[18] sterically hindered phenols,[19] various aromatic amines,[20-23] and certain heterocyclic compounds.[20,21,24-27]

The formation of RC has been most often demonstrated by the usual spectroscopic methods. In a series of reactions of activated aromatic compounds with nitrating agents, RC were isolated preparatively in the form of salts with weakly nucleophilic anions[22,27-29] (Table 1). The formation of extremely unstable RC, such as, for example, the RC derived from toluene (its lifetime in 2 M $HClO_4$ solution is less than 3.3×10^{-7} s [30]) by these procedures is difficult or impossible. An indirect sign of the formation of such species is the presence

in the reaction product of biaryls (dehydrodimers), which usually arise on dimerisation of the RC: [20,31]

$$2ArH^{+\cdot} \rightarrow \overset{+}{A}r(H) - \overset{+}{A}r(H) \rightarrow Ar - Ar + 2H^+$$

An alternative reaction, which also leads to biaryls, involves the attack on the substrate by the arenium cation ArH_2^+ or $ArHNO_2^+$. [32–34]

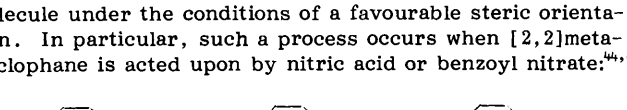
Table 1. The yield of radical-cations in reactions involving the one-electron oxidation of aromatic compounds by nitrating agents.

ArH	Nitrating agent	Solvent	W*, %	Method of determination	Refs.
Phenothiazine	HNO_3	CH_3CN	70	spectrophotometry	[20]
Phenothiazine	HNO_3	$HClO_4$	78	isolation of RC salt	[20]
N-Methylphenothiazine	HNO_3	$ClCH_2CH_2Cl$	35	stopped flow method	[21]
Phenoxazine	HNO_3	CH_3COOH	80	spectrophotometry	[20]
Dibenzo-*p*-dioxin	HNO_3	CF_3COOH	95	spectrophotometry	[25]
NN-Dimethyl-9,10-dihydrophenazine	HNO_3	$ClCH_2CH_2Cl$	97	spectrophotometry	[21]
NNN'N'-Tetramethyl-*p*-phenylenediamine	HNO_3	$ClCH_2CH_2Cl$	85	spectrophotometry	[21]
NNN'N'-Tetramethylbenzidine	HNO_3	CH_3CN	10	spectrophotometry	[20]
Tri-*p*-tolylamine	HNO_3	$ClCH_2CH_2Cl$	79	spectrophotometry	[21]
N-Methylcarbazole	HNO_3	$HClO_4$	95	from the yield of the biaryl RC	[40]
N-Methylcarbazole	HNO_3	CF_3COOH	24	from the yield of biaryl	[20]
1,3-Diphenyl-2-pyrazoline	HNO_3	$HClO_4$	97	from the yield of the biaryl dication	[40]
1,3,5-Triphenyl-2-pyrazoline	NO_2BF_4	CH_3CN	30	from the yield of biaryl	[23]
NN-Dimethylaniline	HNO_3	$HClO_4$	66	from the yield of the biaryl dication	[22]
NN-Dimethylaniline	NO_2BF_4	CH_3CN	12	from the yield of the biaryl dication	[23]
6-Methoxy-1,3-dimethyl-1,2-diaza-1*H*-phenalene	$NaNO_2$	CH_3COOH	75	isolation of the RC salt	[27]

*The yield of the RC estimated from the maximum observed concentration of the RC in the ArH–nitrating agent system or the preparative yield of the RC salt or biaryl. In the last case, the yield is quoted on the assumption that the biaryl is formed as a result of the dimerisation of the RC.

Biaryls are formed as side or main products in the nitration of alkylbenzenes, [35–37] diphenylene, [38] furan, [39] 9-methylcarbazole, [20,40] *NN*-dimethylaniline, [22,31,41] aminonaphthalenes, [42] and derivatives of 1-phenyl-2-pyrazoline [20,40] and 2-acetyl-1-phenylpyrazolidine. [43] It has been established that dehydrodimerisation of alkylbenzenes proceeds without the involvement of the protonated form of the hydrocarbons. [36]

The "cross linking" of the aromatic nuclei under nitration conditions occurs also when they are fragments of a single molecule under the conditions of a favourable steric orientation. In particular, such a process occurs when [2,2]metacyclophane is acted upon by nitric acid or benzoyl nitrate: [44,45]



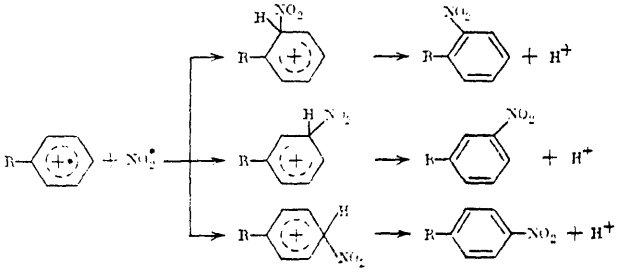
(I)

The initial stage in these reactions leads in all probability to the oxidation of compound (I) to the RC, since it is known [46–48] that the RC of [2,2]metacyclophanes are readily converted into tetrahydropyrenes. Analogous processes have been observed [49] also in the nitration of [3,2]metacyclophanes.

The one-electron oxidation of aromatic compounds by nitrating agents constitutes in many instances an independent reaction leading to the formation of RC as the final product, sometimes in a nearly quantitative yield [25,27,28,40] (Table 1).

2. The Conversion of the Radical-Cations of Aromatic Compounds into Nitro-Compounds

The RC are converted into nitro-derivatives when they are acted upon by nitrogen dioxide [formed in Ar–H–oxygen compounds of nitrogen(V) systems as a result of the reduction of the nitrating agent by the substrate] or the nitrite ion. In the latter case, the initial stage of the reaction is usually the one-electron reduction of the RC by the nucleophile: [50–52]



$$ArH^{+\cdot} + NO_2^- \rightarrow ArH + NO_2^{\cdot}$$

$$ArH^{+\cdot} + NO_2^{\cdot} \rightarrow ArNO_2 + H^+$$

$$2ArH + 3NO_2^{\cdot} \rightarrow 2ArNO_2 + NO^{\cdot} + H_2O$$

The recombination of the RC with $NO_2^{\cdot}$ should be regarded as a special case of little investigated reactions of the following type: [53–58]

$$ArH^{+\cdot} + R^{\cdot} \rightarrow ArHR^+ \rightarrow ArR + H^+$$

The RC dimerisation processes are related to these reactions. [50,59] The results of studies of the interaction of the RC with nitrogen dioxide, carried out mainly in recent years, will be examined below.

Initially an attempt was made to achieve the reactions of RC with nitrogen dioxide by subjecting aromatic compounds to one-electron oxidation (chemical or electrochemical) in the presence of $NO_2^{\cdot}$. The nitration of naphthalene [60] and mesitylene [61] observed under these conditions was interpreted as a result of the recombination of the RC of the hydrocarbons with nitrogen dioxide in accordance with the scheme

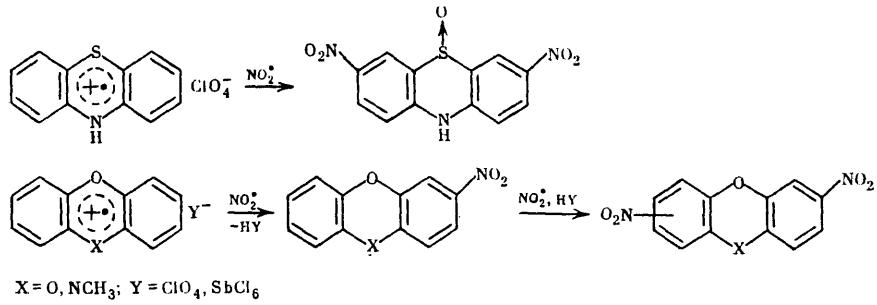
$$ArH \xrightarrow{[Ox]} ArH^{+\cdot}$$

$$ArH^{+\cdot} + NO_2^{\cdot} \rightarrow ArHNO_2^+ \rightarrow ArNO_2^{\cdot} + H^+$$

[Ox] = $Ce(NH_4)_2(NO_3)_6$, or the anode; ArH = naphthalene or mesitylene.

However, the quantitative oxidation of the initial compounds to the RC was not ensured under these conditions, since the hydrocarbons reacted too slowly with the one-electron oxidants. [62] They underwent much faster direct nitration by nitrogen dioxide, which is catalysed by the strong acids accumulating in the $ArH–NO_2^{\cdot}–[Ox]$ system. This process has in fact been the source of nitroarenes (at least of the bulk of the latter). [62] Thus the data quoted above [60,61] neither confirmed nor disproved the possibility of the recombination of the RC with nitrogen dioxide.

Unambiguous evidence for the ability of the RC to react with $NO_2^{\cdot}$ was obtained using stable RC. [22,25,51,63,64] It was found that even RC with a comparatively low reactivity are capable of reacting with $NO_2^{\cdot}$ to form nitro-compounds. The objects of studies were the perchlorates of the RD derived from phenothiazine, [63] *N*-methylphenoxazine, [22] the hexachloroantimonate of the RC obtained from dibenzo-*p*-dioxin, [25] and the hexafluorophosphates of the dimeric RC derived from naphthalene, [51] mono- and di-methylnaphthalenes, [64] pyrene, [64] and perylene. [52] In the case of the first three RC (the reactions were carried out in acetonitrile), nitro-products corresponding to attack on the RC at positions with the maximum unpaired electron density were obtained: [25,65]



X = O, NCH_3; Y = ClO_4, $SbCl_6$

The direct nitration of the corresponding heterocyclic compounds leads to analogous results.[22,25,63]

Table 2. The selectivity of the direct nitration of hydrocarbons of the naphthalene series (ArH) and of the recombination of the corresponding dimeric RC of the type $(ArH)_2^+$ with nitrogen dioxide.[64]

ArH	Nitration conditions	Yields of products of mononitration of ArH in individual positions, %					Distribution of spin density in RC
		1	2	4	5	8	
Naphthalene	A	97—98	2—3	—	—	—	C (1) > C (2)
	E	91	9	—	—	—	
1-Methylnaphthalene	A	—	8	88	1	3	C (4) > C (5) >
	B	—	18	66	10	6	> C (8) > C (2)
	C	—	31	56	8	5	
2-Methylnaphthalene	A	84	—	10	3	3	C (1) > C (8) >
	B	65	—	17	7	9	> C (4) > C (5)
	C	56	—	16	11	12	
1,4-Dimethylnaphthalene	A	—	95	—	5	—	C (5) > C (2) > C (6)
	B	—	3	—	5	—	
	C	—	6	—	18	—	
1,8-Dimethylnaphthalene	A	—	8	92	—	—	C (4) > C (2) > C (3)
	B	—	12	88	—	—	
	C	—	70	30	—	—	
	D	—	21	79	—	—	
2,3-Dimethylnaphthalene	A	90	—	—	10	—	C (1) > C (5) > C (6)
	B	77	—	—	21	—	
	C	77	—	—	18	—	
2,6-Dimethylnaphthalene	A	90	—	10	—	—	C (1) > C (4) > C (3)
	B	78	—	22	—	—	
	C	84	—	15	—	—	

Note. A) An excess of the RC salt was treated with nitrogen dioxide in CH_2Cl_2 at −70—−20 °C; B) nitration of ArH with nitrogen tetroxide in CH_2Cl_2 at 20 °C; C) nitration of ArH with acetyl nitrate in acetic anhydride at −30 °C; D) nitration of ArH with nitric acid in acetic acid at 25 °C; E) nitration with nitronium tetrafluoroborate in CH_2Cl_2 at 25 °C.

The dimeric RC obtained from hydrocarbons of the naphthalene series recombine with $NO_2^\cdot$ to form mixtures of mononitro-derivatives, which have the same qualitative composition as the products of the direct nitration of the corresponding hydrocarbons,[64] for example:

$$(C_{10}H_8)_2^{\cdot+}\,PF_6^- + NO_2^\cdot \rightarrow \alpha\text{-}C_{10}H\text{-}NO_2 + \beta\text{-}C_{10}H_7NO_2 + C_{10}H_8 + HPF_6\,.$$

The quantitative compositions of the nitration products differ significantly in the two cases (Table 2). Compared with the direct nitration, the reactions of dimeric RC with $NO_2^\cdot$ are usually distinguished by greater regioselectivity. However, the RC of 1,4-dimethylnaphthalene gives rise to a high yield of 1,4-dimethyl-2-nitronaphthalene, whereas the nitration of 1,4-dimethylnaphthalene with acetyl nitrate or nitrogen tetroxide usually results in the preferential formation of the 5-nitro-derivative and the products of nitration in the methyl group. It must be emphasised that the conditions of the direct nitration of naphthalene hydrocarbons and their dimeric RC (temperature, acidity of the medium, composition of the ions present, etc.) have frequently differed significantly, which precludes in many instances final conclusions concerning the identity or non-identity of the regioselectivity of the two processes.

Monomeric RC of the naphthalene series are much more reactive than the dimeric RC.[66,67] One can therefore expect that they will recombine with $NO_2^\cdot$ faster than the dimeric RC and with a lower regioselectivity, which, however, may approach the selectivity of the usual nitration of naphthalene and its methyl derivatives. Unfortunately, an experimental test of this hypothesis is hindered by the extreme instability of this RC.

It has been suggested[64] that the reactivity of the RC with respect to $NO_2^\cdot$ decreases sharply with decrease in the electrochemical oxidation potentials of the corresponding ArH and of the RC of aromatic substrates having potentials less than 1.7 V relative to the normal hydrogen electrode do not interact with nitrogen dioxide. However, it has been shown[68] that the rates of reaction of the stable RC of tri-*p*-anisylamine and tri-*p*-bromophenylamine with an N_2O_4 solution are approximately the same despite the very large difference between the oxidation potentials of the corresponding amines (~0.7 V). The effective rate constants are 0.33 and 0.25 litre$^{1/2}$ mol$^{-1/2}$ s^{-1} at 20 °C (the reactions are of first order with respect to RC and of order 0.5 with respect to N_2O_4). Furthermore, the RC of tri-*p*-tolylamine proved to be much more reactive than the RC of tri-*p*-bromophenylamine (by a factor of 10^2),[68] whereas under conditions where the oxidation-reduction potential of the ArH/ArH^+ pair plays a decisive role one would expect the opposite relative reactivities of these RC. One cannot rule out the possibility of a parallel variation of the reactivity of the RC with respect to nitrogen dioxide and of their tendency to dimerise with formation of doubly protonated iaryls.

Nothing is known at present about the rate of reaction of highly active short-lived RC with $NO_2^\cdot$ in solution, but it has been established that in the gas phase such reactions are very rapid. The rate constant for the recombination of the dimeric RC derived from benzene with nitrogen dioxide is 2.4×10^{-11} cm^3 molecule^{-1} s^{-1} under these conditions.

The monomeric RC of toluene and *p*-xylene react somewhat more slowly and the reaction of the RC of naphthalene is much slower.[69,70]

The joint anodic oxidation of 1,4-dimethoxybenzene and the nitrite anion yielded 1,4-dimethoxy-2-nitrobenzene,[71] whose formation was explained by the recombination of the RC of 1,4-dimethoxybenzene with nitrogen dioxide:

$$p\text{-}CH_3OC_6H_4OCH_3 \xrightarrow{-e} p\text{-}CH_3OC_6H_4OCH_3^{+\cdot},$$

$$NO_2^- \xrightarrow{-e} NO_2^{\cdot},$$

$$p\text{-}CH_3OC_6H_4OCH_3^{+\cdot} + NO_2^{\cdot} \xrightarrow{-H^+} CH_3O\text{-}C_6H_3(NO_2)\text{-}OCH_3.$$

A parallel variation of the ease of substitution of a particular hydrogen atom by the nitro-group on treatment with $NO_2^{\cdot}$ and of the unpaired electron density at the corresponding carbon atom has been observed for the dimeric RC of naphthalene and 1,8-, 2,3-, and 2,6-dimethylnaphthalenes (see Table 2). More or less pronounced deviations from this type of variation occur for the RC of other naphthalene hydrocarbons.[64] These data justify the hypothesis that the distribution of the unpaired electron density on the RC is an important but not the only factor determining the isomeric composition of the nitro-products formed from the RC and nitrogen dioxide.

Table 3. Comparison of data for the nitration of aromatic compounds and the distribution of unpaired electron density in their RC.

ArH	Position in ArH at which nitration occurs preferentially	Position with maximum unpaired electron density in the RC
Benzonitrile	3 [74]	3 [75]
Nitrosobenzene	4 [76]	3 [77]
Benzoic acid	3 [74]	3 [75]
Toluene	4 [74]	4 [78]
Anisole	4 [74]	4 [79]
NN-Dimethylaniline	4 *	4 [80]
4,*NN*-Trimethylaniline	2 *	2 [81]
4-Methoxy-*NN*-dimethylaniline	2 *	2 [81]
4-Acetamido-*NN*-dimethylaniline	2 *	2 [81]
4-Carboxy-*NN*-dimethylaniline	2 *	2 [81]
4-Formyl-*NN*-dimethylaniline	2 *	2 [81]
4-Nitro-*NN*-dimethylaniline	2 *	2 [81]
4,4-Bis(dimethylamino)benzophenone	3 *	3 [81]
NNN'N'-Tetramethylbenzidine	3 [82]	3 [83]
Diphenylamine	4 *	4 [80]
Triphenylamine	4 [84, 85]	4 [80]
Naphthalene	1 [86]	1 [87]
Anthracene	9 [88]	9 [89]
Pyrene	1 [90]	1 [91]
Perylene	3 [92]	3 [89]
Azulene	1 [93]	1 [94]
Biphenylene	2 [38]	2 [95]
Furan	2 [96]	2 [97]
Pyrrole	2 [96]	2 [97]
Thiophen	2 [96]	2 [97]
Benzo-*p*-dioxin	2 [98]	2 [24]
Phenothiazine	3 [99]	3 [65]

*The data were taken from the handbook "Beilsteins Handbuch der organischen Chemie", Vierte Verlage, Springer Verlag, Berlin.

Note. Numbers in square brackets denote references (Ed. of Translation).

The partial addition of $NO_2^{\cdot}$ to the *unco*-positions in the RC apparently has an appreciable influence on the ratio of the nitro-isomers formed in a number of instances. Evidently, in such cases a greater or smaller proportion of the nitration products should be formed from the *unco*-σ-complex and the isomeric composition of the nitro-product does not reflect the true reactivities of the individual positions in the RC.

It is of interest to trace also the relation between the distribution of the unpaired electron density in the RC $ArH^{+\cdot}$ and the position of the nitro-group in the nitration of ArH, such relation having been postulated previously.[72,73] The data in Table 3 (see also Table 2) show that the situation in this case is analogous to that examined above for the dimeric RC of the naphthalene series. Here too the most probable cause of the absence of an unambiguous relation between the unpaired electron density in the RC and the position of the nitro-group is the formation in the nitration reaction of *unco*-σ-complexes, which mask the true reactivities of the different positions in the ArH.[11] The complicating influence of this factor is apparently minimal for the positions in the ArH corresponding to the maximum unpaired electron density in the RC (Tables 2 and 3) and as a rule aromatic compounds are nitrated preferentially precisely in these positions. This rule can evidently be used to predict the positional selectivity in electrophilic aromatic nitration reactions.

One may predict the existence also of other factors which disturb the relation between the unpaired electron density in the RC and the positional selectivity of the nitration reaction. One of these factors can be seen in the nitration of secondary aromatic amines. *N*-Nitramines, which are converted into products of the nitration of the aromatic ring via the nitramine rearrangement, are intermediates in such reactions.[100] The preferential nitration of the amine in the *o*-position relative to the amino-group is usually a consequence of this mechanism,[101] although the unpaired electron density in the RC of aromatic amines is as a rule a maximum in the *p*-position (see Table 3). The unexpected nitration of nitrosobenzene in the *p*-position (in its RC, the unpaired electron density is a maximum in the *m*-position) is in all probability associated with the occurrence of the reaction via the intermediate formation of the hydrated form of the substrate.[102]

The coincidence of the most reactive position in the aromatic compound with the site where the maximum unpaired electron density is located in the RC, usually observed, creates additional possibilities for predicting the characteristic features of the electronic structure of the RC on the basis of data for the nitration of the corresponding ArH. For example, the nitration of vinylarenes in an unsaturated substituent[103,104] indicates an increased unpaired electron density in the vinyl group in the RC of vinylarenes. This is also indicated by the anomalous character of the dimerisation of such RC (unlike other RC of the type $ArH^{+\cdot}$, they dimerise via the exocyclic β-carbon atoms[105,106]) and by the result of a quantum-chemical calculation for the styrene RC.[107]

In the nitration of *m*-disubstituted benzenes in which one substituent is a powerful *ortho*- and *para*-directing agent and the other is a *meta*-directing agent, the influence of electron-donating substituents usually predominates.[108] It is natural to expect that the unpaired electron density in the RC of the aromatic compounds indicated will be a maximum in the *o*- and *p*-positions relative to the electron-donating group. The available data show that this is indeed the case. For example, for the RC of *NN*-dimethyl-3-nitroaniline,[81] the hyperfine interaction constant, which is directly proportional to the spin density is 5.9 and 6.3 G respectively for the *o*- and *p*-positions relative to the dimethylamino-group, while for the *m*-position it does not exceed 1.8 G.

The data examined indicate the possibility, in principle, of nitration via the intermediate formation of the RC, because they demonstrate that aromatic compounds can be converted

under the nitration conditions into the RC and the latter can be converted into nitro-compounds.

III. NITRATION OF AROMATIC COMPOUNDS BY THE NITRONIUM CATION

1. Nitration in the Gas Phase

Being a powerful oxidant,† the nitronium cation in the gas phase readily abstracts a single electron from the molecules of aromatic compounds such as benzene and its derivatives, converting them into the RC.[70,110] The subsequent recombination of the products of the one-electron transfer leads to a σ-complex, which is deprotonated on collision with molecules of bases B, forming the nitro-product.[70,111] Direct addition of the nitronium cation to benzene and its derivatives does not occur under these conditions:[70]

$$ArH + NO_2^+ \rightarrow ArH^{+\cdot} + NO_2^{\cdot} \rightarrow ArHNO_2^+ \xrightarrow[-BH^+]{B} ArNO_2$$

(here and henceforth B represents the base.) The electron transfer occurs in virtually every collision of the reacting species. The radical recombination stage is significantly slower and limits the rate of formation of the σ-complex.[70] The data presented confirm the validity of the quantum-chemical calculations,[7,112,113] indicating the possibility of electron transfer in nitration by the nitronium cation.

Thus, in the gas-phase nitration of aromatic compounds, the substrate RC is the primary reaction product and the σ-complex is the secondary product.

2. Nitration in Solution

The oxidising properties of the nitronium cation in solution can be characterised by the $NO_2^{\cdot}/NO_2^+$ oxidation-reduction potential, which is ~1.6 V in acetonitrile[114,115] and ~1.9 V in nitromethane[116] (relative to the normal hydrogen electrode). The rate of nitration of aromatic compounds by the nitronium cation increases with decrease in the ionisation potential, reaching a limit which is determined by the diffusion of the reacting species.[72,117] On the basis of the data of Coombes et al.,[117] the limiting ionisation potential can be estimated as being of the order of 8.8–9.0 eV.

The question of the mechanism of the liquid-phase nitration by the nitronium cation is at present controversial. Many experimental data obtained in the study of this reaction can be explained satisfactorily by a heterolytic mechanism in which the initial stage is the formation of the π-complex $ArH...NO_2^+$ with the nitro-group located at one of the π-bonds of the aromatic ring.[118] However, facts also exist which provide grounds for the hypothesis that the reaction can proceed via electron transfer.[9,13,60,74,113,118,119]

Perrin's communication,[60] which has aroused a lively discussion, quotes a number of arguments in support of the occurrence of this stage in the nitration of aromatic substrates more reactive than toluene by the nitronium cation. According to this study,[60] the reaction mechanism includes in this instance the formation of the short-lived radical pair $[ArH^{+\cdot}NO_2^{\cdot}]$ and its geminal recombination in the solvent cage:

$$ArH + NO_2^+ \rightarrow [ArH^{+\cdot}NO_2^{\cdot}] \rightarrow \underset{\sigma\text{-complex}}{ArHNO_2^+} \xrightarrow[-BH^+]{B} ArNO_2$$

One of the main arguments in support of this mechanism is that naphthalene is nitrated to give the usual mixture of mononitronaphthalenes in its oxidation at the anode in the presence of nitrogen dioxide.[60] It has been suggested that the nitration of naphthalene in the given instance is a result of the recombination of the naphthalene RC formed at the anode with $NO_2^{\cdot}$. However, it was soon established that this process proceeds virtually without the participation of the electrochemically generated RC.[62]

According to Eberson and Radner,[115] the nitration by the nitronium cation proceeds preferentially via the heterolytic (polar) pathway and only to an insignificant extent via the radical-ion pathway involving the outer-sphere electron transfer. It has also been suggested that, firstly, the relative contributions of these reaction pathways depend on the $ArH/ArH^{+\cdot}$ oxidation-reduction potential, and secondly, that the homolysis of the σ-complexes is an additional source of the $ArH^{+\cdot}$ RC and, thirdly, that the regioselectivities of the attack on ArH by the nitronium cation and on $ArH^{+\cdot}$ by nitrogen dioxide are in general different:

$$ArH + NO_2^+ \begin{cases} \rightarrow ArH^{+\cdot} + NO_2^{\cdot} \\ \downarrow\uparrow \\ \rightarrow ArHNO_2^+ \xrightarrow[-BH^+]{B} ArNO_2 \end{cases}$$

Consequently, some of the nitro-products are formed, according to Eberson and Radner,[115] via the following reaction sequence:

$$\underset{(A)}{ArHNO_2^+} \rightarrow ArH^{+\cdot} + NO_2^{\cdot} \rightarrow \underset{(B)}{ArHNO_2^+} \rightarrow ArNO_2$$

where (A) and (B) are mixtures of isomeric σ-complexes differing in their composition. For this nitration pathway, the positions of the nitro-groups will be determined by the free-radical recombination stage and the set of the first two stages can be regarded as a kind of variant of the inner-sphere electron transfer.[120] There are a series of arguments in support of this view.

(1) The selectivity in the nitration of naphthalene by nitronium tetrafluoroborate ($\alpha/\beta \cong 15$) is not identical with the selectivity in the reaction between the dimeric napthalene RC and nitrogen dioxide ($\alpha/\beta \cong 40$).[51]

(2) The rate constants for the outer-sphere electron transfer from ArH to NO_2^+, calculated using the Marcus equation,[115] are much smaller than the corresponding rate constants for the nitration of ArH. The calculated constants depend on the $ArH/ArH^{+\cdot}$ oxidation-reduction potentials and vary within extremely wide limits (from ~10^{-16} litre mol^{-1} s^{-1} for benzene to ~10^6 litre mol^{-1} s^{-1} for ferrocene).

(3) The attempts to observe the chemically induced dynamic nuclear polarisation in nitration by the nitronium cation were unsuccessful.[121,122]

The different selectivity of the nitration in the $C_{10}H_8$–NO_2^+ and $(C_{10}H_8)_2^{+\cdot}$–$NO_2^{\cdot}$ systems apparently mean that the dimeric RC does not participate significantly in the nitration of naphthalene by the nitronium cation. However, this fact by itself does not justify the confident conclusion that the more reactive[66,67] monomeric naphthalene RC does not participate in the above reaction, because the selectivity in its recombination with nitrogen dioxide is unknown and there is no reason to suppose that it should be the same as that for the dimeric RC. Account must also be taken of the complex formation reaction between the nitronium cation and the solvent,[123,124] the decrease in the reactivity of NO_2^+ induced by this phenomenon (approximately by an order of magnitude[123]),

† The electron affinity of the nitronium cation can be estimated as being above 9 eV on the basis of the ionisation potential of nitrogen dioxide.[109]

and a probable change in the geometrical configuration of NO_2^+ on which the results of calculations of the rate constant for electron transfer between ArH and NO_2^+ depend decisively. It is also essential to take into account data[125] from which it follows that the rates of nitration of aromatic comounds by the nitronium cation may be appreciably lower than has usually come to be assumed (for example, at least by two orders of magnitude in the case of anisole).

The homolysis of σ-complexes is indeed possible. However, it is doubtful if this reaction can serve as an effective source of RC in the ArH–NO_2^+ systems: examination of data for the chemistry of the $ArHNO_2^+$ cation[126–132] creates the impression that these species are incapable of homolysis occurring readily enough to be able to compete with their deprotonation to nitro-derivatives.

According to Fukuzumi and Kochi,[74] like other electrophilic aromatic substitution reactions, nitration by the nitronium cation begins with the formation of a charge-transfer complex (CTC) between the reacting species, in which inner-sphere electron transfer takes place subsequently from the substrate of the reactant. The electron transfer is then regarded as a consequence of the thermal electronic excitation of the CTC, and the electronically excited state of the CTC is identified as the radical pair $[ArH^+E^\cdot]$:

$$ArH + E^+ \rightarrow ArH\cdots E^+ \xrightarrow{h\nu} [ArH^+E^\cdot] \rightarrow \underset{\sigma\text{-complex}}{ArHE^+} \rightarrow ArE + H^+$$

where E is the electrophile, including NO_2^+.

In particular, the linear dependence of the activation energy for electrophilic substitution on the energy of the charge-transfer bands in the spectrum of the complex $ArH\ldots E^+$ and also of the reaction constants ρ in the Brown equation on the quantities $\Delta h\nu_{st}/\Delta I$ characterising the rate of variation of the energy of the charge transfer band ($h\nu_{st}$) with the ionisation potential I of ArH supports this mechanism.[74]

The electron transfer mechanism described is analogous to that proposed previously.[133–136] From the standpoint of the ideas of the above investigators,[74,133–136] the thermal transfer of an electron thus proceeds analogously to its phototransfer. The most important difference consists in the fact that the electron phototransfer, being a Franck–Condon process, leads to the formation of a radical pair in a non-equilibrium unrelaxed state and therefore requires a much greater energy expenditure than the thermal transfer.[74,136–138] Comparison of the ArH/ArH^+ and $NO_2^\cdot/NO_2^+$ oxidation-reduction potentials[115] shows that, for aromatic compounds with low ionisation potentials, the energy levels of the complexes $ArH\ldots NO_2^+$ and $ArH^+\ldots NO_2^\cdot$ should be similar or that their ratio should be actually reversed.

The main reason why the calculation of the rate constants for the outer-sphere electron transfer from ArH to NO_2^+ leads to unduly low values of the latter is the appreciable energy of the reorganisation of the NO_2 group necessary for the electron transfer.[115] The component associated with the change in the internuclear angles of the NO_2 fragment on transition from the linear nitronium cation to the bent nitrogen dioxide molecule makes the dominant contribution to this energy. The unfavourable influence of this factor is apparently markedly weakened in electron transfer via the inner-sphere mechanism, since there is reason to believe that the NO_2 group then passes from the linear to the angular state already in the complex formation stage.[139] In general, the transition from the outer-sphere to the inner-sphere mechanism is frequently accompanied by a marked increase in the rate of electron transfer (up to by a factor of 10^9 [140]).

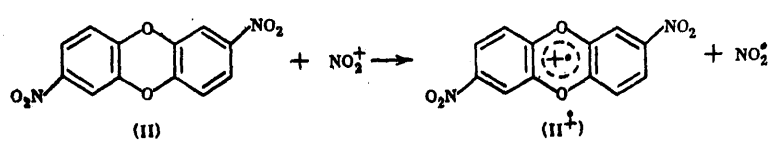
For aromatic amines, sulphides, and ethers, there exists yet another pathway to the formation of the radical pair $[ArH^+NO_2^\cdot]$, which has apparently not been discussed in the literature. The molecules of these compounds are attacked by the nitronium cation in the first place at the heteroatom having an unshared electron pair.[141] The homolysis of the ammonium, sulphonium, and oxonium cations formed under the conditions can evidently lead to the radical pair indicated:

$$ArXR_n + NO_2^+ \rightarrow Ar\overset{+}{X}R \rightarrow ArXR_n^+ + NO_2^\cdot$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad NO_2$$
$$X = N, O, S$$

The experimental confirmation of the possibility of the one-electron oxidation of aromatic compounds in the ArH–NO_2^+ system is hindered by the low stability of the RC, their ability to recombine with $NO_2^\cdot$, and, in particular, by the fact that in the case of the most active RC the recombination of the radical pairs $[ArH^+NO_2^\cdot]$ can apparently occur in the solvent "cage" without the emergence of the radicals into the bulk of the solution.

Examples of the oxidation of aromatic substrates to the RC by nitronium tetrafluoroborate have been described,[18,23,25] but one cannot be certain that the nitronium cation is in fact the oxidant in these reactions, since the reactant usually contains an admixture of the nitrosonium cation, which is difficult to separate and which is capable of oxidising these substrates

The results obtained for 2,7-dinitrodibenzo-*p*-dioxin (II) are of interest in this connection.[142] When compound (II) is treated with nitric acid in concentrated sulphuric acid, the radical-cation (II^+) is formed. Under these conditions, the nitrosonium cation does not oxidise the dioxin (II). Consequently a one-electron oxidant, superior in its strength to the nitrosonium cation, exists in the HNO_3–H_2SO_4 system (or can be formed in the presence of ArH). Since nitric acid is almost fully converted into the nitronium cation (the most reactive oxygen compound of nitrogen) under the conditions indicated above, it was concluded that the cation is responsible for the oxidation of the dioxin (II) to the RC:[142]



(II) (II^+)

The reaction discovered is the most convincing of experimental evidence for the ability of aromatic compounds to be oxidised in solution to the RC by the nitronium cation.

One can thus conclude that the role of the electron transfer in liquid-phase reactions involving the nitration of aromatic compounds by the nitronium cation is less clear than in the gas-phase reaction. However, here too there can be hardly any doubt about the possibility of the intermediate formation of the RC. Nevertheless the question of the extent to which the RC participates in these reactions is general and must still be regarded as open.

IV. CATALYTIC NITRATION

We shall now consider another large group of nitration reactions—the reactions occurring without the participation of the nitronium cation and catalysed by nitrous acid.# This nitration pathway is characteristic of aromatic compounds having fairly low ionisation potentials and activated with respect to electrophilic substitution.[3] The catalytic nitration reactions frequently occur under autocatalytic conditions, since the nitration catalyst is usually formed in the course of the reaction itself. In a pure form, they occur in media containing virtually no nitronium cations.

The mechanism of the catalytic reaction is often described in terms of a scheme involving nitration via nitrosation:[3]

$$ArH + HNO_2 \rightarrow ArNO + H_2O$$
$$ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2, \text{ etc.}$$

It has been suggested that the initial formation and subsequant accumulation of nitrous acid in the ArH–HNO_2 systems occur as a result of the reduction of nitrous acid in oxidation-reduction side reactions. However, a number of experimental data, in particular the intermediate formation of the σ-complexes of $ArHNO_2^+$ in certain autocatalytic reactions[144,145] and also the preferential nitration of phenol in the *o*-position on treatment with dilute nitric acid (the nitrosation of this compound takes place almost exclusively in the *p*-position[146]) cannot be explained satisfactorily within the framework of this mechanism. Furthermore, there exist quite a few activated aromatic compounds§ whose nitrosation is unknown and many of them apparently do not enter into this reaction at all. Nevertheless, such compounds usually readily undergo autocatalytic nitration.

It has been shown recently that the autocatalytic nitration of *NN*-dimethylaniline[31] and phenol[147]—the classical substrates in the nitrosation reaction—and also naphthalene[148] cannot be explained in terms of the nitration mechanism involving reaction via nitrosation, at least in strong acids.

Two mechanisms are nowadays considered as the most probable. Firstly, one mechanism involves catalytic nitration initiated by the one-electron oxidation of the substrate,[31,40,145,148,149] whose possibility is due to the ability of the lower oxygen compounds of nitrogen ("nitrous acid") to effect the one-electron oxidation of activated aromatic compounds. The second mechanism involves nitration in which the active species is the electrophile $N_2O_4.NO^+$,[64] formed from nitrogen tetroxide and the nitrosonium cation.

The subsequent Sections will deal with the reactions involving the one-electron oxidation of aromatic compounds by the nitrosonium cation, their role in the formation of RC in the ArH–HNO_3 system and in autocatalytic nitration, and also the mechanism of nitration with participation of $N_2O_4.NO^+$.

1. The Nitrosonium Cation as a One-Electron Oxidant in Reactions with Aromatic Compounds

Until recently, the possibility of the one-electron oxidation of aromatic compounds by the nitrosonium cation had hardly been taken into account. This cation was regarded exclusively as a nitrosating agent interacting with aromatic substrates via a heterolytic mechanism. The limitations of this treatment became clear in recent years when the ability of the nitrosonium cation to accept one electron from the molecules of aromatic compounds has been demonstrated:

$$ArH + NO^+ \rightarrow ArH^+ + NO^\cdot$$

Reactions of this type were initially observed for readily oxidisable ArH of the amine type, namely phenothiazine,[150] phenoxazine,[40,151] *NNN'N'*-tetramethyl-*p*-phenylenediamine,[21] and derivatives of 9,10-dihydrophenazine.[21] It was later shown that polycyclic aromatic hydrocarbons also react similarly with NO^+.[18,22,115,152,153] For example, on reaction with nitrosonium perchlorate in trifluoroacetic acid, naphthalene is converted initially into the monomeric RC, then into the dimeric RC, and finally into a mixture of hydrocarbons having the polynaphthylene structure:[152,153]

$$C_{10}H_8 + NO^+ \rightarrow C_{10}H_8^+ + NO^\cdot$$
$$C_{10}H_8^+ + C_{10}H_8 \rightarrow (C_{10}H_8)_2^+$$
$$(C_{10}H_8)_2^+ \rightarrow \rightarrow C_{10}H_7 - (C_{10}H_6)_n - C_{10}H_7$$

In contrast to readily oxidisable substrates, naphthalene reacts with the nitrosonium cation fairly slowly, which can be explained by the endoergic character of the electron transfer in this case (calculation yields $\Delta G_0 = 13.1$ kcal mol^{-1} [115]). The reaction can be conveniently followed from the evolution of nitric oxide, whose yield is ~90% with respect to the initial nitrosonium salt.[153] These data show that the nitrosonium cation is almost incapable of nitrosating naphthalene.

Fluorene, triphenylmethane, and thiophen also interact with nitrosonium perchlorates with liberation of nitric oxide,[153] which indicates the one-electron oxidation of the substrates in these cases too. It is of interest that *NN*-dimethylaniline—an aromatic compound which readily undergoes electrophilic nitrosation—behaves in relation to the nitrosonium cation primarily as a one-electron reductant.[22,31]

Calculations by the Marcus equation of the thermodynamic kinetic characteristics of processes involving the one-electron oxidation of aromatic compounds by the nitrosonium cation[115] support the view that the formation of the RC is a result of the direct electron transfer from the π-system of the substrate to the electrophile.

Aromatic compounds of the benzen-type, which are oxidised with difficulty, hardly interact with the nitrosonium cation under the usual conditions (if one disregards the formation of a charge-transfer complex).[154,155] Calculations have shown[115] that the inertness of the nitrosonium cation with respect to such substrates is mainly due to thermodynamic causes (the oxidation-reduction equilibrium is very strongly displaced towards ArH and NO^+). It is therefore not surprising that the hexafluorophosphate of the hexafluorobenzene RC readily

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All the lower oxygen compounds of nitrogen analytically determined as nitrous acids are designated for convenience by the term "nitrous acid".[143] The nitrosonium cation has come to be regarded as the most reactive component of nitrous acid.

§ Here and henceforth, this term is used to designate compounds containing aromatic nuclei activated with respect to electrophiles (aromatic amines, alkoxyarenes, polycyclic arenes, etc.).

reacts with nitric oxide, oxidising it to the nitrosonium cation:[156]

$$C_6F_6^+PF_6^- + NO^\cdot \rightarrow C_6F_6 + NO^+PF_6^-$$

In the gas phase the oxidising properties of the nitrosonium cation are more pronounced than in solutions and under these conditions it readily oxidises benzene to the RC.[157,158] The appreciable weakening of the oxidising properties of NO^+ in solution compared with the gas phase is caused by its strong solvation (the calculated hydration energy of NO^+ is ~80 kcal mol^{-1} [159]).

Other lower oxygen compounds of nitrogen can in all probability also function as one-electron oxidants in relation to aromatic compounds, because they frequently possess pronounced oxidising properties. For example, the electron affinity of nitrogen dioxide (3.1 eV [160]) is close to the electron affinity of powerful oxidants such as chlorine and bromine, while the calculated standard oxidation-reduction potential of the $NO_2^-/NO_2^\cdot$ pair is ~1 V in water.[161]

2. Autocatalytic One-Electron Oxidation of Aromatic Compounds by Nitric Acid

When aromatic compounds are oxidised to the RC by dilute nitric acid, which contains hardly any nitronium cations, the nitrosonium cation usually functions as the one-electron oxidant.[22,31,40,145,151,162] Reactions of this type are autocatalytic and are characterised by an induction period. The latter factor is caused by the absence of the nitrosonium cation from the reaction mixture in the initial period of the interaction. A special case of these reactions are those described by the overall equation[22,40,151]

$$3ArH + HNO_3 + 3H^+ \rightarrow 3ArH^+ + NO^\cdot + 2H_2O \quad (1)$$

For example, the oxidation of phenothiazine and phenoxazine by nitric acid in 57% perchloric acid, which leads to the RC perchlorates and nitric oxide in 75–80% yield, proceeds in accordance with this scheme.[40,151] Reactions (1) usually occur as independent reactions for the stoichiometric reactant ratio or in the presence of a deficiency of nitric acid. When an excess of HNO_2 is used, the nitration of ArH is usually observed.[22,28,29,40] The relatively unreactive forms of nitrous acid do not play a significant part in the oxidation of ArH, because in strong acids, where reactions (1) were carried out, they are converted into the nitrosonium cation.[163]

The reduction of dilute nitric acid by activated aromatic compounds is apparently similar to the cathodic reduction of this reactant, which is also autocatalytic.[164] Reactions (1) can be regarded as a kind of chain process in which the chain propagation stage is described by Eqns.(2) and (3):[40,165]

$$ArH + NO^+ \rightarrow ArH^+ + NO^\cdot \quad (2)$$

$$NO^\cdot + 0.5HNO_3 + 1.5H^+ \rightarrow 1.5NO^+ + H_2O \text{ , etc.} \quad (3)$$

The multiplication coefficient of the one-electron oxidant (NO^+) in this scheme is 1.5, which ensures the occurrence of one-electron oxidation with self-acceleration. The initial formation of the nitrosonium cation in the reaction mixture and hence the chain initiation take place in all probability as a result of the reduction by the aromatic substrate of the nitronium cation present at a vanishingly low concentration.

Eqn.(3) describes the autocatalytic regeneration of the nitrosonium cation from nitric oxide, which is the reverse of disproportionation of nitrous acid.[166,167] This process is catalysed by nitrous acid and proceeds with intermediate formation of nitrogen dioxide.[167]

In the case of unstable RC, the autocatalytic oxidation of ArH in accordance with Eqn.(1) is masked by the subsequent reactions of these radicals, for example, by their dimerisation. Dimeric products are obtained in the oxidation of *NN*-dimethylaniline,[22,31] 9-methylcarbazole,[40] and 1,3-diphenyl-2-pyrazoline [40] by nitric acid. As an example, we shall consider the reaction of *NN*-dimethylaniline with HNO_3 in 57% perchloric acid, which leads to the *NNN'N'*-tetramethylbenzidinium dication (IV) and nitric oxide in yields of ~80%:[22]

$$3C_6H_5N(CH_3)_2 + HNO_3 + 3H^+ \rightarrow 3C_6H_5\overset{+}{N}(CH_3)_2 + NO^\cdot + 2H_2O$$

$$2C_6H_5\overset{+}{N}(CH_3)_2 \rightarrow (CH_3)_2N\text{–}C_6H_4\text{–}C_6H_4\text{–}N(CH_3)_2 + 2H^+$$

(III)

$$3\,(III) + 2HNO_3 + 6H^+ \rightarrow 3\,(CH_3)_2\overset{+}{N}{=}C_6H_4{=}C_6H_4{=}\overset{+}{N}(CH_3)_2 + 2NO^\cdot + 4H_2O$$

(IV)

The overall reaction equation is

$$6C_6H_5N(CH_3)_2 + 4HNO_3 + 6H^+ \rightarrow 3\,(IV) + 4NO^\cdot + 8H_2O$$

Anthracene reacts with nitric acid in 57% perchloric acid in a manner different from that of the reactions of *NN*-dimethylaniline, 9-methylcarbazole, and 1,3-diphenyl-2-pyrazoline, affording anthraquinone as the final product. The initial stage of the reactions is probably the same as for the compounds quoted above:[22]

$$3C_{14}H_{10} + HNO_3 + 3H^+ \rightarrow 3C_{14}H_{10}^+ + NO^\cdot + 2H_2O$$

This is supported by the formation of nitric oxide from nitric acid in a high yield. The anthracene RC is converted into anthraquinone as a result of its interaction with water in the presence of an excess of the oxidant.[168–170] The ability of NO^+ to oxidise anthracene to the RC has been established.[115] An analogous interpretation of the formation of anthraquinone in the nitration of anthracene with nitrogen tetroxide has been given in another study.[171]

The analogy between the autocatalytic one-electron oxidation of activated aromatic compounds by nitric acid and the reactions involving the oxidation of certain inorganic substances by the same reagent is striking. The dissolution of metallic silver on interaction with nitric acid in 57% perchloric acid[40] and the oxidation of bivalent iron to the tervalent state[172] can serve as examples of such processes:

$$3Ag + HNO_3 + 3H^+ \rightarrow 3Ag^+ + NO^\cdot + 2H_2O$$
$$3Fe^{2+} + HNO_3 + 3H^+ \rightarrow 3Fe^{3+} + NO^\cdot + 2H_2O$$

3. Autocatalytic Nitration Initiated by One-Electron Oxidation

The mechanism of nitration of this type involves two couple stages: the autocatalytic oxidation of the aromatic compound to the RC and the conversion of the RC into the nitro-produc as a result of its recombination with nitrogen dioxide.[31,40,145,148,165] The autocatalytic character of these reactions therefore arises in the one-electron oxidation stage, in the course of which an electron is transferred from the aromatic substrate to the nitrosonium cation or to some other form of nitrous acid.

When the conditions in the interaction of the reactants do not favour the recombination of the RC with nitrogen dioxide, the reactions occurring in the ArH–HNO_3 system are restricted to the one-electron oxidation of the aromatic compound. As already mentioned, the formation of the nitroproducts is promoted by the use of an excess of nitric acid.

Such influence by the excess of the reagent can be accounted for by the increase in the concentration of nitrogen dioxide in the reaction mixture as a consequence of the more effective absorption of nitric oxide by nitric acid. In the ideal case, where they entire nitric oxide formed in accordance with Eqn.(1) is oxidised to the dioxide, the one-electron oxidation of ArH can be described by Eqn.(4) and the autocatalytic nitration can be described by Eqns.(4) and (5):

$$ArH + HNO_3 + H^+ \rightarrow ArH^{+\cdot} + NO_2^{\cdot} + H_2O \quad (4)$$

$$ArH^{+\cdot} + NO_2^{\cdot} \rightarrow ArNO_2 + H^+ \quad (5)$$

According to the literature,[31,149] the autocatalytic nitration reactions initiated by the one-electron oxidation are of first order with respect to the substrate, although a fractional order has been quoted (1.5).[148] The order with respect to nitric acid is variable, diminishing with increase in its concentration from 1 to 0.[31,148,149] This finding has been explained by the change of the rate-limiting stage when the reactant concentration is altered. At higher concentrations, the electron transfer from ArH to the one-electron oxidant becomes such a stage, while at low concentrations the oxidation of nitric oxide by nitric acid becomes rate-limiting.

The mechanism of the autocatalytic nitration initiated by the one-electron oxidation corresponds to a true autocatalytic process, since in this case the accumulation of the catalyst does not require the occurrence of any side reactions. In this respect, it differs from the mechanism involving nitration via nitrosation, in which the accumulation of nitrous acid can be achieved only as a result of side reactions.

The nitration of *NN*-dimethylaniline by nitric acid in 75–80% sulphuric acid is an example of an autocatalytic reaction which exhibits a number of specific features.[31] These include a fairly high concentration of the nitronium cation in the reaction mixture and the complete protonation of the initial amine. The reaction products are mainly *NN*-dimethyl-*p*-nitroaniline and nitroderivatives of *NNN'N'*-tetramethylbenzidine in proportions which depend on the acidity of the medium. The base, formed apparently as a result of the unusual deprotonation of the protonated amine by the nitrosonium cation, enters into the reaction.[31] A nitration mechanism with participation of not only the nitrosonium cation but also of the nitronium cation has been proposed:

It is noteworthy that this mechanism can be only specific in character. In principle, it is applicable solely to the nitration of sufficiently basic aromatic compounds which are almost wholly protonated under the reaction conditions. If the reaction mixture contains an appreciable concentration of the non-protonated substrate, then evidently in this case the substrate can react mainly with the nitronium cation, which is more reactive as an electrophile than the nitrosonium cation by ~14 orders of magnitude.[173]

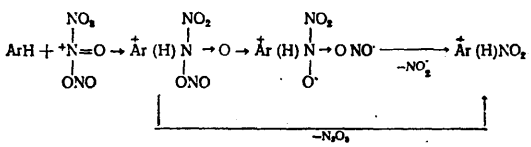
The products of the autocatalytic nitration of *NN*-dimethylaniline,[174] *p*-nitrophenol,[175,176] mesitylene,[122] and durene[177] (labelled with $H^{15}NO_3$ nitric acid) in sulphuric or trifluoroacetic acid exhibit a chemically induced dynamic polarisation of the ^{15}N nuclei, which has been explained by the formation of nitro-derivatives from the radical pairs $[ArH^{+\cdot}NO_2^{\cdot}]$.

There is now no doubt that the autocatalytic one-electron oxidation of ArH can be the initial stage of the autocatalytic nitration of activated aromatic compounds.

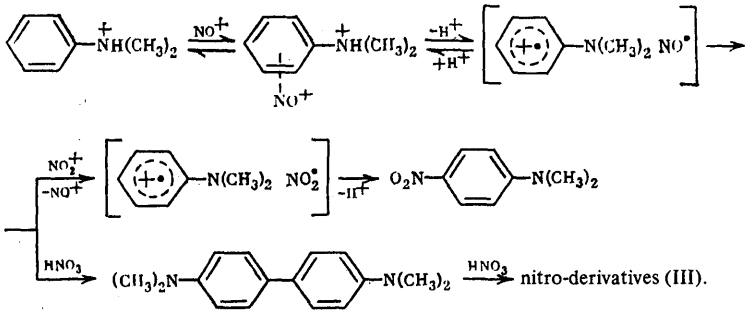
4. The Mechanism of the Autocatalytic Nitration with Participation of $N_2O_4.NO^+$

A new mechanism has been proposed recently for the autocatalytic nitration catalysed by the cation $N_2O_4.NO^+$ [64,178] whose existence has not so far been confirmed. It is assumed that this cation, tentatively formed from nitrogen tetroxide and the nitrosonium cation, is directly involved as the nitrating species:

$$N_2O_4 + NO^+ \rightarrow N_2O_4 \cdot NO^+$$



$$\overset{+}{Ar}(H)NO_2 + N_2O_3 \rightarrow ArNO_2 + HNO_2 + NO^+$$



nitro-derivatives (III).

(III)

The oxidation of nitrous acid by nitric acid regenerates nitrogen tetroxide (and hence also the catalyst). The above mechanism explains the chemically induced dynamic nuclear polarisation effect in the catalytic nitration reactions by the intermediate formation of radical pairs in the homolysis of the primary σ-complex at the N–O bond.

The determination of the applicability of the mechanisms examined evidently required further studies. Nevertheless, it is already clear that the mechanism involving nitration via nitrosation can be excluded from consideration for catalytic nitration reactions of a number of aromatic hydrocarbons (for example, naphthalene), since such compounds are either hardly nitrosated or they react with nitrosating agents too slowly.

V. THE CHANGE IN THE MODE OF REACTION AFTER A CHANGE IN THE REACTANT RATIO

As already mentioned, in certain cases the use of a deficiency of the nitrating agent makes the RC of the substrate the final product of the reaction of the latter. This is associated with the uncoupling of the multistage radical-ion nitration process in the part of the mechanism between the first and subsequent stages, which is induced by unfavourable conditions for the conversion of the RC into the nitration product. The influence of this factor decreases rapidly with increase in the mole fraction of the reactant in the initial reaction mixture. This can result in an additional change in the composition of the reaction product corresponding to the transition from the one-electron oxidation to nitration after a comparatively small change in the reactant ratio.[22,25,28,29]

A characteristic example is provided by the nitration of dibenzo-*p*-dioxin (V) in trifluoroacetic acid.[25] For the reagent : substrate molar ratio $n \geq 2$, this compound reacts rapidly with nitric acid, being converted into a mixture of 2,7-dinitrodibenzo-*p*-dioxin (VI) and 2,8-dinitrodibenzo-*p*-dioxin (VII) in a high yield. The nitration is accompanied by the appearance of a rapidly vanishing blue colour characteristic of the RC ($V^{+\cdot}$). On the other hand, for $n = 0.3–0.5$, the RC is the final reaction product (in ~90% yield). The range of values of n from 2 to 0.5 corresponds to a smooth transition from nitration to one-electron oxidation:

For a specified value of n, variation of the concentrations of the starting materials does not entail significant changes in the ratio of the RC and the nitro-compounds.

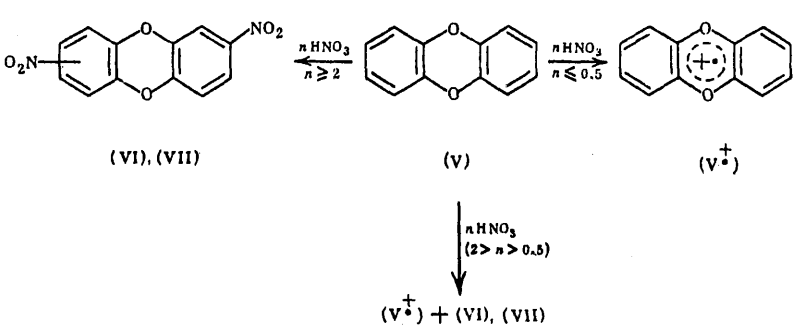
The fact that the dinitro-derivatives (VI) and (VII) are also formed in the presence of a deficiency of nitric acid implies that the introduction of the second nitro-group is faster than that of the first. This anomaly can apparently be explained by the higher reactivity of the RC of the mononitro-derivative of dioxin compared with ($V^{+\cdot}$) under conditions where the introduction of both groups is limited by the rates of recombination of the above RC with $NO_2^{\cdot}$.

A mixture of the dinitro-compound (VI) and (VII) is obtained also in the reaction of a known salt of the radical-cation ($V^{+\cdot}$) with nitrogen dioxide.[25] The introduction of the second nitro-group is undoubtedly catalysed in this case by the strong acid formed in the RC mononitration stage (cf. Eberson et al.[62]).

In the nitration of compound (V) by nitrogen tetroxide in trifluoroacetic acid, the same features are observed as in the nitration with nitric acid.[25] For the reagent : substrate molar ratio $n = 0.25$, the RC ($V^{+\cdot}$) formed is stable, while for $n \geq 1.5$, it is converted into a mixture of the nitro-compounds (VI) and (VII) in a high yield. The values of n between 0.25 and 1.5 constitute an intermediate region. The limiting value $n = 1.5$ corresponds to the stoichiometry of the dinitration of aromatic compounds by nitrogen tetroxide.[25,179]

A radical-ion mechanism has also been proposed for the nitration of aromatic compounds by nitrogen tetroxide in neutral solvents. It has been suggested that the initial stage of the nitration involving this mechanism is the oxidation of the substrate to the RC by nitrogen dioxide.[171] However, it has been suggested[64] that the operation of this mechanism is unlikely because nitrogen dioxide is a poor one-electron oxidant (the electron exchange in the $NO_2^{\cdot}$–NO_2^- system is relatively slow). The formation of the RC when aromatic compounds having pronounced reducing properties are acted upon by nitrogen tetroxide can be explained[64] by the oxidation of ArH by the nitrosonium cation arising as a result of the isomerisation of N_2O_4 to the nitrosyl nitrate form.

A dependence of the composition of the reaction product on the reagent : substrate ratio, analogous to that examined above, obtains also in the nitration of phenothiazine,[28,29] *N*-methylphenoxazine,[22] and probably *NN*-dimethylaniline[22] by nitric acid.



VI. NITRATION OF AROMATIC COMPOUNDS BY TETRANITROMETHANE AND METAL NITRATES

1. Thermal Nitration by Tetranitromethane

Tetranitromethane (TNM) is a mild nitrating agent[180] and a moderately strong oxidant (electron affinity 1.3 eV,[180] electrochemical reduction potential in methanol 0.7 V,[181] calculated oxidation-reduction potential in water 0.9 V relative to the normal hydrogen electrode[182]).

The interaction of aromatic compounds with TNM begins in all probability with electron transfer from the substrate to the reagent within the ArH...TNM CTC:

$$ArH + C(NO_2)_4 \rightarrow ArH\cdots C(NO_2)_4 \rightarrow ArH^{+}\,C(NO_2)_4^{-}$$

The decomposition of the TNM radical-anion formed leads to nitrogen dioxide,[180] which subsequently reacts with the RC and the excess substrate:

$$C(NO_2)_4^{-} \rightarrow C(NO_2)_3^{-} + NO_2^{\cdot}$$

$$ArH^{+} + NO_2^{\cdot} \xrightarrow{-H^{+}} ArNO_2$$

The rate-limiting stage of the nitration can be both electron transfer and the conversion of the RC into the nitro-product. The latter variant is most favourable for demonstrating the reaction mechanism and obtains in the case of the least active RC.

An example of the reactions in which electron transfer is not the rate-limiting stage is provided by the nitration of *N*-methylphenoxazine (VIII).[22,26] In this reaction, the initial aromatic compound is oxidised rapidly and with a high yield to the RC, which is subsequently converted comparatively slowly into *N*-methyl-3-nitrophenoxazine (IX).

The Figure presents the spectra of the (VIII)–TNM system in the visible region, demonstrating the conversion of the RC into the nitro-compound. The presence of the isosbestic point confirms the conclusion that the RC is located on the nitration coordinate. The nitro-compound (IX) can also be obtained by treating a known salt of the RC (VIII^{+}) with nitrogen dioxide or TNM.[22]

It is noteworthy that the reaction of the oxazine (VIII) with TNM is the first example of nitration where direct evidence has been obtained for the intermediate formation of the substrate RC and it has been shown that this nitration pathway is the main one.

The reactions of TNM with the phenyl derivatives of magnesium, tin, and mercury are also of the oxidation-reduction type, but in this case the aromatic compounds are hardly nitrated. The main product of these reactions is benzene.[183,184] The above finding has been explained by the specific properties of the organometallic RC, namely by their ability to fragment readily with formation of neutral free radicals.[183,184] The fragmentation is so rapid that there is insufficient time for the RC to recombine with nitrogen dioxide:

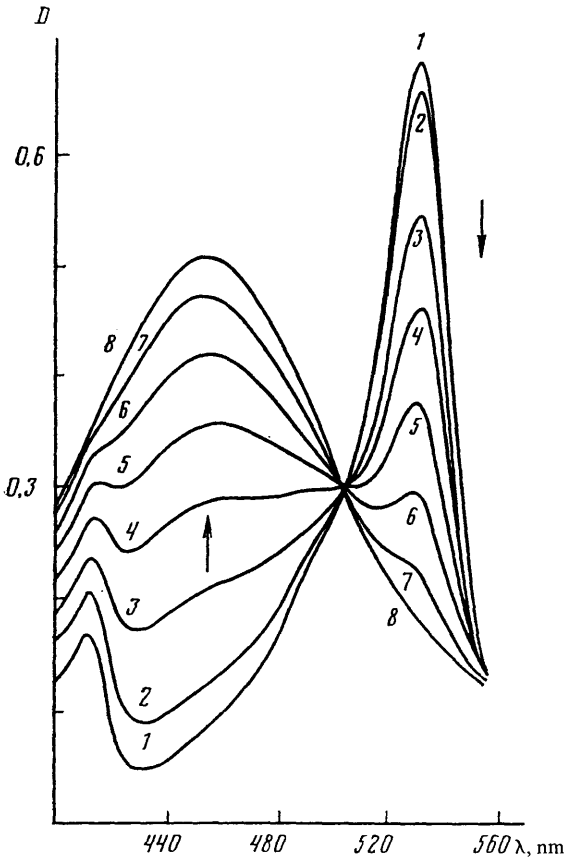
$$C_6H_5M + C(NO_2)_4 \rightarrow C_6H_5M^{+} + C(NO_2)_4^{-} \rightarrow C_6H_5^{\cdot} + M^{+}C(NO_2)_3^{-} + NO_2^{\cdot}$$

$$C_6H_5^{\cdot} \xrightarrow{Solv} C_6H_6$$

$$C_6H_5^{\cdot} + NO_2^{\cdot} \rightarrow C_6H_5NO_2$$

$M = C_6H_5Mg,\ C_6H_5Hg,\ (C_6H_5)_3Sn$; Solv = solvent.

The low yield of nitrobenzene indicates a low probability of the recombination of the radicals $C_6H_5^{\cdot}$ and $NO_2^{\cdot}$ in solutions.[183,184]



Electronic absorption spectra describing the conversion of the *N*-methylphenoxazine RC into *N*-methyl-3-nitrophenoxazine on nitration of *N*-methylphenoxazine with TNM in 97% acetic acid.[22] The absorption band with λ_{max} = 412 and 533 nm are due to the RC and that at 450 nm is due to the nitro-derivative. The initial concentrations of the reagent and the substrate were 5×10^{-3} and 5×10^{-4} M respectively; the thickness of the cell l = 0.1 cm. Spectra recorded under the following conditions: 1) 1 min after mixing the initial solutions; 2) after 2.5 min; 3) after 21 min; 4) after 51 min; 5) after 1 h 27 min; 6) after 2 h 7 min; 7) after 2 h 54 min; 8) after 3 h 53 min.

2. Photochemical Nitration with Tetranitromethane

Under the usual conditions, TNM does not react with aromatic compounds difficult to oxidise such as benzene, naphthalene, etc. or reacts with them very slowly.[185] However, it readily forms charge-transfer complexes with these compounds, whose irradiation with light at the wavelength corresponding to the charge-transfer band leads to the electron transfer:[186]

$$ArH + C(NO_2)_4 \rightarrow ArH\cdots C(NO_2)_4 \xrightarrow{h\nu} [ArH^{+}C(NO_2)_3^{-}] + NO_2^{\cdot}$$

One may therefore expect that nitration of the relatively unreactive ArH would be accelerated in the light. It has been shown for *N*-ethylcarbazole [187] that such influence by light does indeed occur.

The photochemical nitration of anthracene with TNM leads to a 9-nitroanthracene, which has been explained by the recombination of the 9-anthryl free radical with $NO_2^{\cdot}$.[188] However, one cannot rule out the possibility that the anthracene RC, whose formation in the course of the reaction is not open to doubt, in contrast to the 9-anthryl radical, participates in the formation of the nitro-derivative together with nitrogen dioxide.[188]

3. Nitration with Metal Nitrates

Among all the metal nitrates, the strongest nitration agents are salts with pronounced oxidising properties[189–196] such as titanium(IV), zirconium(IV), iron(III), and copper(II) nitrates and cerium ammonium nitrate. Some of these salts are such powerful oxidants that under the usual conditions they oxidise even alkanes[193] and water.[195]

The study of the nitration of aromatic compounds with titanium(IV) nitrate led to the conclusion that the nitrate salt is involved directly in the reaction.[191] Under comparable conditions, anhydrous metal nitrates can be superior to nitric acid as regards their nitrating capacity.[191,192] These facts indicate that nitration with metal nitrates can proceed via a specific mechanism and not necessarily via a trivial pathway involving the hydrolysis of the salt.

According to a recently proposed mechanism,[197] in the nitration of arenes by cerium ammonium nitrate,[192] the nitronium cation, formed in the interaction of the initial compounds, is the active species. Together with nitration, the oxidation of arenes to the RC by the cerium(IV) cation,[198] which is regarded as a side reaction,[197] has also been noted. However, the question of the role of the RC in such reactions and even more so in nitration by metal nitrates is not in general quite so simple, because there is a possibility of the formation of nitro-products from the RC when they interact with nitrate anions:

$$ArH + M(NO_3)_n \rightarrow ArH^{+}NO_3^{-} + M(NO_3)_{n-1}$$
$$ArH^{+} + NO_3^{-} \rightarrow \rightarrow ArNO_2$$

Such a nitration mechanism has been proposed in a study[199] of the nitration of *N*-methylphenoxazine (VIII). Heating of this compound in propanol with iron(III) or copper(II) nitrate leads to a satisfactory yield of the 3-nitro-derivative (IX). The formation of the phenoxazine RC is observed in the cold. The known radical-cation salt ($VIII^{+}\cdot ClO_4^{-}$) also gives rise to the nitro-compound (IX) on heating in propanol with tetrapropylammonium or potassium nitrate.

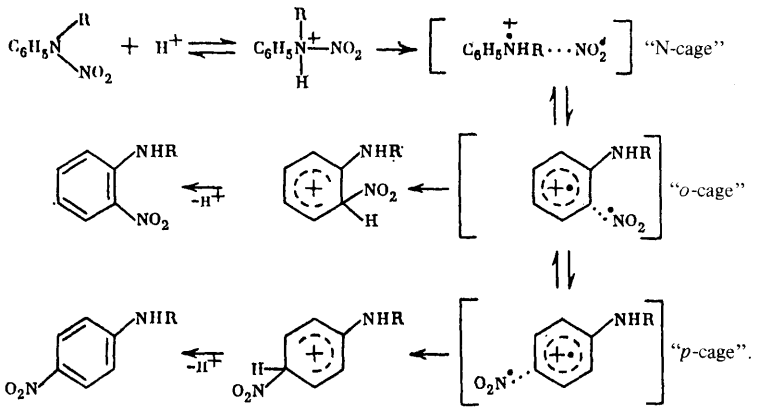
A number of facts indicate indirectly that this nitration pathway is possible also for other aromatic compounds. For example, it has been shown that the one-electron oxidation of benzene by cobalt(III) trifluoroacetate in the presence of potassium nitrate leads to nitrobenzene.[200] The electrochemical oxidation of anthracene in the presence of the tetrabutylammonium nitrate supporting electrolyte as the potential corresponding to the oxidation of anthracene to the RC affords a mixture of 9-nitro-, 9,10-dinitro-, and 4,9-dinitro-anthracene.[201] Under these conditions, the supporting electrolyte is oxidised only at an appreciably higher potential.

Although the mechanism of the conversion of the RC into nitro-compounds on interaction with NO_3^{-} is as yet not clear, the very fact of the occurrence of such reactions is not open to doubt. One of them has been described in a study[202] where it was shown, in an investigation of the action of nucleophiles on the RC of dibenzo-*p*-dioxin, that treatment of the perchlorate salt of this RC with potassium nitrate leads to 2-nitrodibenzo-*p*-dioxin. In contrast to the RC of dibenzo-*p*-dioxin, the thianthrene RC, which has a similar structure, reacts with the nitrate anion to form thianthrene *S*-oxides.[203]

The nitration of aromatic compounds by palladium nitrate proceeds via a specific mechanism, which is indicated by the unusually high level of *m*-substitution in the nitration of toluene and chlorobenzene by this reagent.[204] The partial rate factors for the attack of toluene by $Pd(NO_3)_2$ are 0.3 (*o*), 1.3 (*m*), and 3.0 (*p*). The partial rate factors for the palladisation of toluene by bivalent palladium salts are close to these values:[205] 0.28–0.95 (*o*), 1.44–1.87 (*m*), and 1.64 to 4.47 (*p*). It is logical to suppose that the nitration of aromatic substrates by palladium nitrate involves the intermediate formation of organopalladium compounds.

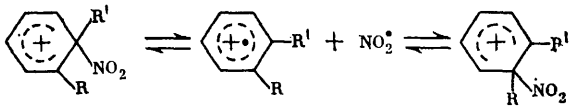
VII. THE RADICAL-ION MECHANISM OF THE NITRAMINE REARRANGEMENT AND THE ISOMERISATION OF NITROARENIUM CATIONS

The radical-ion mechanism of the nitramine rearrangement, involving the homolysis of the protonated form of nitramine with formation of the amine RC and nitrogen dioxide followed by the recombination of these radicals, has been justified in a number of studies:[206–209]



This mechanism is supported by the observation of the CIDNP effect in one of the reactions of the type considered[210] and also by the results of measurements of the $^{15}N/^{14}N$ and $^{14}C/^{12}C$ kinetic isotope effects.[211]

The isomerisation of the nitroareneium cations $ArRNO_2^+$ with the migration of the nitro-group along the perimeter of the aromatic ring is usually regarded as an intramolecular process.[132] However, one cannot rule out the possibility that in certain cases it can proceed via a radical-ion pathway similar to the mechanism of the nitramine rearrangement:[60]



From the standpoint of thermodynamics, the homolysis of nitroarenium cations is preferable to the alternative pathway involving their dissociation into ArH and NO_2^+ in those cases where the ArH have fairly low ionisation potentials. This conclusion is based on the results of the calculation of the ΔG_0 corresponding to electron transfer from various aromatic compounds to the nitronium cation.[115] The possibility of the radical-ion pathway leading to the isomerisation of nitroarenium cations is supported by data for the capacity for homolysis.[212] However, it is not as yet clear whether this reaction pathway can be the main one.

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Thus studies in recent years have shown that the ideas about electrophilic nitration according to which it is a purely heterolytic process can no longer claim to be universal. An increasing number of facts have been appearing which do not fit within the framework of these ideas and which show that radical species such as radical-cations and nigrogen dioxide can play an important role in nitration. On the other hand, these facts do not conflict with the classical mechanism of nitration as regards the role of the σ-complexes as the direct precursors of the nitro-derivatives. For practical purposes, it is extremely significant that free radicals serve as a source of not only nitro-products but also (by virtue of their high reactivity) of various side products. It is not difficult to note that the observed evolution of ideas about the nitration mechanism is a specific manifestation of the more general trend towards a separation of the concepts of heterolytic and electrophilic (nucleophilic) substitution. As a result, the fact that a reaction belongs to the class of electrophilic (nucleophilic) substitution reactions is no longer a basis for its automatic inclusion in the series of heterolytic reactions. In the field of nucleophilic aromatic substitution reactions, this has been reflected, in particular, by the establishment of the $S_{RN}1$ radical-nucleophilic substitution mechanism.

The studies designed to discover the role of electron transfer in nitration are naturally far from being completed. One can suppose that they will ultimately lead to the development of clear experimental criteria for a radical-ion mechanism and will provide an answer to the question of its specific contribution in the overall set of aromatic nitration reactions.

During the preparation of the article for publication, a series of new studies concerning the role of the oxidation-reduction stage in nitration reactions have been published, in particular a monograph[213] and a review,[214] which contain sections devoted to these reactions. It has been shown[215] that the regioselectivity of the nitration of naphthalene with nitric acid in trifluoroacetic acid, expressed by the ratio α : β of the mononitronaphthalenes formed, depends significantly on temperature and, when the latter is reduced, it reaches values characteristic of the recombination of the dimeric naphthalene radical-cation with nitrogen dioxide. This fact and also the detection of the radical-cation indicated above in the $C_{10}H_8$–HNO_3–CF_3COOH system have been interpreted as evidence for the radical-ion mechanism of the nitration of naphthalene.

The complex oxidation reactions occurring in the interaction of a series of compounds of the dihydropyridine series with nitric acid have been explained by the oxidation of these compounds to the RC and the recombination of these species with nitrogen dioxide via the oxygen atom of the latter.[216]

The mechanism of the nitration of aromatic compounds by nitrogen tetroxide, whose initial stage is the heterolysis of N_2O_4 to form the nitrosonium cation, has been discussed.[217] Other pathways leading to nitration by this reagent presumably involve its homolysis to nitrogen dioxide. The latter can oxidise aromatic substrates to the RC,[218,219] which, as already mentioned, are capable of being converted into nitrocompounds under the influence of $NO_2^{\cdot}$. It has been demonstrated by pulse methods[218,219] that the electron transfer from *NNN'N'*-tetramethylbenzidine, *N*-methylphenothiazine, and metiazinic acid to $NO_2^{\cdot}$ in polar medium is extremely fast: the corresponding rate constants are of the order of 10^7–10^8 litre mol^{-1} s^{-1}. According to the available data,[178] there is also a possibility of the free-radical attack on aromatic substrates by nitrogen dioxide, characterised by a low positional selectivity and also leading to nitro-derivatives.

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Selenonium Compounds and Their Applications in Synthesis

N.N.Magdesieva

The review gives a systematic account and surveys the results of studies in the chemistry of selenonium compounds (salts, ylides, ylide-salts, diylides, and imides). The methods of synthesis of selenonium compounds, their structure, their behaviour in reactions with electrophiles and nucleophiles, and also their reactions under conditions of thermolysis and rearrangements are considered.
The bibliography includes 95 references.

CONTENTS

I. Introduction 161
II. Selenonium salts 161
III. Unstabilised and monostabilised selenium ylides 163
IV. Distabilised selenium ylides 165
V. Bis-onium selenium compounds 168
VI. Selenimides 170

I. INTRODUCTION

Selenonium compounds contain a fragment with a tricoordinate positively charged selenium atom; they include selenoxides, selenimides, selenonium salts, selenium ylides, and also bis-onium compounds (ylide-salts and di-ylides) containing, together with the selenonium fragments, also fragments based on other heteroatoms (nitrogen, phosphorus, arsenic, and sulphur). The present review does not include data from the chemistry of selenoxides, because the reactivity of the latter has been described in detail in a series of reviews published in recent years.[1-3]

The sharp growth of interest in the chemistry of selenonium compounds (salts, ylides, and ylide-salts) in recent years is due to their ready availability and high reactivity, which as a rule greatly exceeds the reactivity of the corresponding sulphonium compounds and in many cases has no analogy in the chemistry of the onium compounds of Group V and VI elements. The interest of chemists in these compounds is associated not only with their importance for theoretical organic chemistry but also with the real possibility of their practical use as convenient active synthons for fine organic synthesis, the majority of the reactions with the participation of which proceed stereospecifically and regioselectively.

This review gives a systematic account and surveys the results of studies on the development of the methods of synthesis, the structures, physicochemical properties, and reactivities of selenonium compounds (salts, ylides, ylide-salts, diylides, and also selenimides) during the last 15 years. Until 1972, the chemistry of these compounds was hardly investigated and there have been only individual studies on the synthesis of selenonium salts, which have been surveyed in a monograph.[4]

Wherever possible, the reactivities of selenonium systems have been compared with sulphur compounds of analogous structure.

II. SELENONIUM SALTS

The first and most general method of synthesis of selenonium salts involves the alkylation of selenides with alkyl halides, α-bromoacids and their esters, and α-bromoketones.

Alkyl diphenylselenonium tetrafluoroborates have been obtained by alkylating diphenyl selenide with alkyl halides in the presence of a stoichiometric amount of silver tetrafluoroborate:[5]

$$Ph_2Se + \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!CHX \xrightarrow{AgBF_4} Ph_2\overset{\oplus}{S}e\text{-}CH\!<\!\begin{matrix} R^1 \\ R^2 \end{matrix}\ \overset{\ominus}{B}F_4$$

$R^1 = R^2 = H$, X = I; $R^1 = H$, $R^2 = Me$, X = Br; $R^1 = R^2 = Me$, X = I

The alkylation of a selenide containing the trifluoromethyl group has been described:[6]

$$PhSeCF_3 \xrightarrow{MeI,\ AgBF_4} Ph\text{—}\overset{Me}{\overset{|}{\overset{\oplus}{S}e}}\text{—}CF_3\ \overset{\ominus}{B}F_4$$

A convenient method of synthesis of selenonium salts containing the benzyl group involves the methylation of selenides with trimethyloxonium tetrafluoroborate and also with methyl fluorosulphonate,[7] for example:

$$RCH_2SePh \xrightarrow{\overset{\oplus}{Me_3}O\ \overset{\ominus}{B}F_4} RCH_2\overset{\oplus}{\underset{|}{S}}ePh\ \overset{\ominus}{B}F_4$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad Me$$

R = Ph, *p*-ClC_6H_4, *m*-ClC_6H_4, *p*-MeC_6H_4.

Unsaturated selenides are smoothly alkylated with methyl fluorosulphonate:[8]

$$\underset{SePh}{\overset{|}{\overset{|}{\text{—CH=C}}}}\!<\!\begin{matrix} R \\ R^1 \end{matrix} \xrightarrow{MeSO_3F} \underset{\oplus SeMe}{\overset{|}{\overset{|}{\text{—CH=C}}}}\!<\!\begin{matrix} R \\ R^1 \end{matrix}\ SO_3^{\ominus}F$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad Ph$$

R = H, Me; $R^1 = C_6H_{13}$, C_8H_{17}

Diaryl selenides are arylated with iodonium salts in the presence of copper(II) benzoate:[9]

$$Ph_2Se + \overset{\oplus}{Ar_2}\overset{\ominus}{I}AsF_6 \xrightarrow{Cu\,(II)} ArPh_2\overset{\oplus}{S}e\ \overset{\ominus}{A}sF_6 + ArI$$

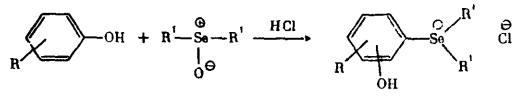
Ar = Ph, *p*-t-BuC_6H_4, *p*-MeC_6H_4, 3,4-$Me_2C_6H_3$

Diaryl selenides readily react with t-butyl hypochlorite:[10]

$$Ar_2Se + t\text{-}BuOCl \rightarrow Ar_2\overset{\oplus}{S}eOBu\text{-}t\ \overset{\ominus}{Cl}.$$

Methods of synthesis of selenonium salts on the basis of organic derivatives of selenium(IV), namely selenoxides, diorganoselenium dihalides, and selenium halides and oxides halides, are known. A method of synthesis of dialkyl- or

alkylphenylhydroxyphenylselenonium chlorides by the reaction of phenols with selenoxides and hydrogen chloride has been developed:[11]



R = Me; R' = Me, Et, Ph

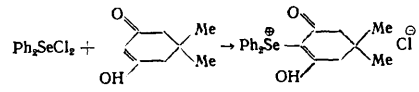
Tri-*p*-tolylselenonium chloride has been obtained by the reaction of toluene with selenium dioxide in the presence of sulphuric acid.[12]

Triarylselenonium salts have been synthesised from selenium oxide chloride and arylmagnesium bromides:[13]

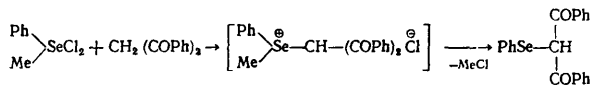
$$RC_6H_4MgCl + SeOCl_2 \xrightarrow{HX} (RC_6H_4)_3\overset{\oplus}{S}e\overset{\ominus}{X}$$

X = Cl, Br, I; R = H, *o*-Me, *m*-Me, *p*-Me.

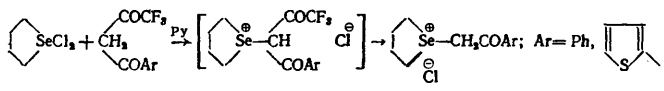
The synthesis of triarylselenonium salts by the reaction of diarylselenium dichlorides with activated arenes has been described.[20] Diphenylselenium dichloride reacts with dimedone to form a selenonium salt. The ease of this reaction is due to the fact that the enolic proton in the fixed *trans*-enol structure of dimedone can promote the polarisation of the Se–Cl bond:[14]



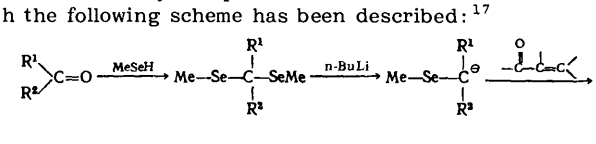
In the reaction of methylphenylselenium dichloride with dibenzoylmethane, the intermediate selenonium salt is demethylated:[15]

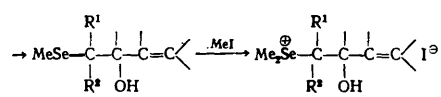


In the case of β-diketones containing the trifluoroacetyl group, the cleavage of the intermediate diketoselenonium salts by a nucleophile (Py or $Cl^{\ominus}$) proceeds differently, which can be accounted for by the large positive charge on the carbonyl carbon atom of the CF_3 group of the diketoselenonium salt:[16]



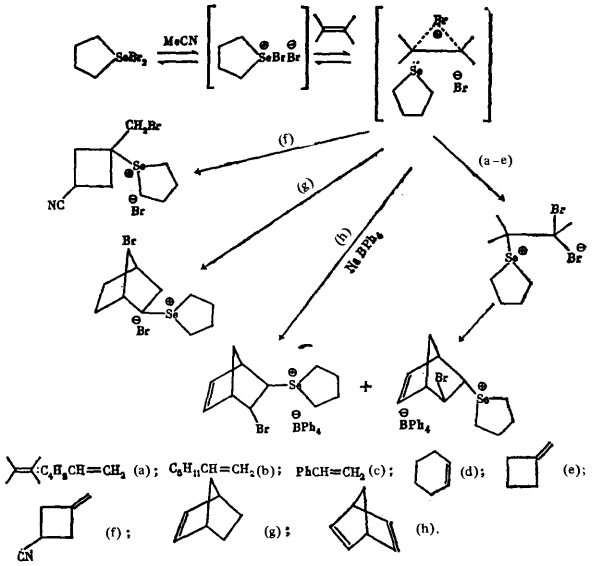
The synthesis of γδ-unsaturated β-hydroxyselenonium salts from carbonyl compounds and a selenol in accordance with the following scheme has been described:[17]





$R^1 = R^3 = H$, Me; $R^1 = H$, R^2 = Me; $R^1 = H$; $R^2 = Me(CH_2)_6$—

A method of synthesis of a new type of selenonium compounds, namely β-bromoselenonium salts, based on the interaction of tetramethylselenium dibromide with olefins having different structures (acyclic, cyclic, and skeletal), has been developed recently.[18] The electrophilic addition of tetramethyleneselenium dibromide to acyclic and cyclic olefins proceeds *trans*-stereospecifically with formation of 2-bromoalkyltetramethyleneselenonium bromides together with dibromoalkanes. The addition of tetramethyleneselenium dibromide to norbornene is accompanied by a rearrangement as a result of a 7,2-hydride shift and the addition to norbornadiene takes place with formation of a 3 : 1 salt mixture comprising 2-*endo*-bromo-3-*exo*-(tetramethyleneselenonium)- and 2-*exo*-bromo-3-*endo*-(tetramethyleneselenonium)-norbornene bromides:

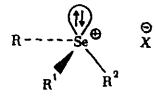


Dinitro-substituted selenonium salts have been obtained by protonating diphenylselenonium dinitromethylide with inorganic acids having a weakly nucleophilic anion:[19]

$$Ph_2\overset{\oplus}{S}e\overset{\ominus}{C}(NO_2)_2 + HX \rightleftharpoons Ph_2\overset{\oplus}{S}eCH(NO_2)_2\,\overset{\ominus}{X}$$

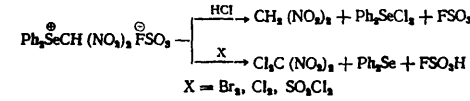
X = SO_3F; BF_4; F

The selenium atom in selenonium compounds is in the sp^3-hybrid state and the selenonium group therefore has a pyramidal structure:



A series of optically active selenonium salts have been obtained, whose stability indicates a high barrier to inversion at the selenonium chiral centre.[21] X-Ray diffraction,[22] UV spectroscopic,[23] IR spectroscopic,[24] and ^{77}Se NMR [25] data as well as the electrical conductivities of aqueous solutions of selenonium salts and the ability of the salts to exchange readily their anions[26] have confirmed their ionic structure. Selenonium tetraphenylborates are soluble in organic solvents, which makes it possible to use them in homogeneous reactions.[27] Selenonium salts with two electron-accepting groups are unstable and readily decompose.[28]

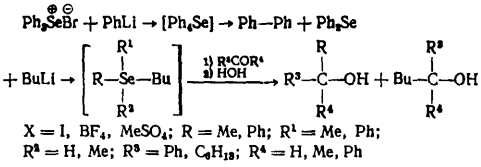
On treatment with electrophiles, diphenyl(dinitromethyl)-selenonium salts are cleaved at the Se–CNO_2 bond:[19]



X = Br_2, Cl_2, SO_2Cl_2

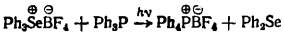
Reactions with nucleophiles are most characteristic of selenonium salts. On treatment with organolithium compounds, the intermediate σ-selenuranes undergo further

reactions: [29]



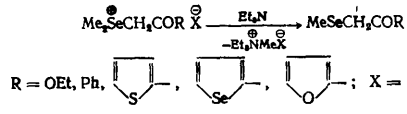
The last reaction can be used to synthesise tertiary alcohols.[29]

The photochemical reaction of triphenylselenonium tetrafluoroborate with triphenylphosphine via a radical mechanism has been described: [30]

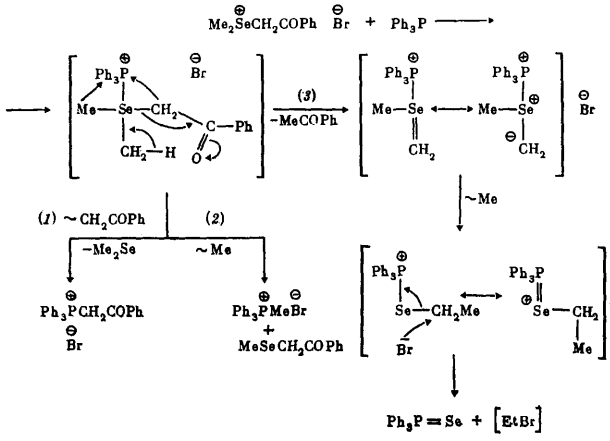


The homolytic character of the dissociation of the bond in the initial selenonium salt is confirmed by the fact that the reaction does not proceed in the dark and that benzene is formed as a side product. [30]

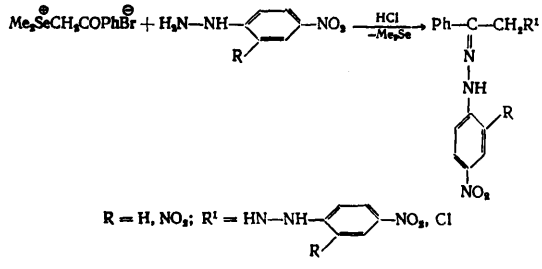
The interaction of arylacyl- and alkoxycarbonyl-methyl-(dimethyl)selenonium salts with nucleophiles (tertiary amines, substituted hydrazines, and triphenylphosphine) has been investigated. The demethylation of selenonium salts with triethylamine, which takes place with formation of α-methylselenocarbonyl compounds, is a convenient method of their synthesis: [27]



The reaction of dimethylphenylacylselenonium bromide with triphenylphosphine apparently proceeds via the primary attack by the nucleophile on the selenium atom with the subsequent migration of the phenylacyl or methyl group from selenium to phosphorus (pathways 1 and 2) and the elimination of acetophenone from the σ-selenurane intermediate (pathway 3): [27]

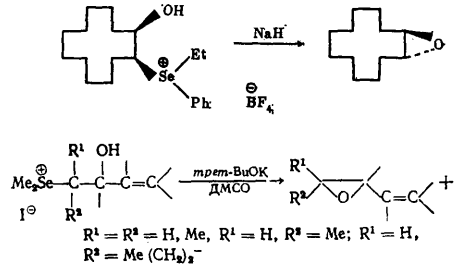


The interaction of dimethylphenylacylselenonium bromide with substituted hydrazines is accompanied by the elimination of dimethyl selenide: [27]



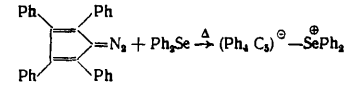
The reactions of selenonium salts with bases are very important. They are the basis of a general preparative method of synthesis of unstabilised selenium ylides and also of monostabilised ylides containing one electron-accepting group at the ylide carbon atom.

Treatment of β-hydroxyselenonium salts with bases results in a stereospecific reaction involving the intramolecular nucleophilic substitution of the selenonium group with formation of epoxides, [33] including αβ-unsaturated epoxides: [17]

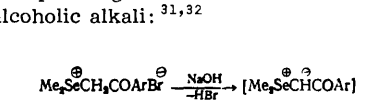


III. UNSTABILISED AND MONOSTABILISED SELENIUM YLIDES

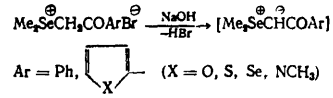
A general preparative method of synthesis of monostabilised selenium ylides involves the interaction of their conjugate acids with bases [31,32] or the decomposition of diazocompounds in the presence of selenides, [33,34] which takes place via the formation of a carbene: [35]



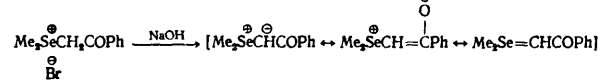
Potassium t-butoxide is normally used to generate unstabilised selenium methylides *in situ*: [6]



Monocarbonyl-stabilised selenium ylides are obtained *in situ* when the corresponding selenonium salts are treated with aqueous or alcoholic alkali: [31,32]

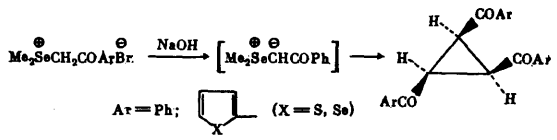


Only one selenium monoketoylide, namely dimethylselenobenzoylmethylide, has been isolated. It is an extremely labile crystalline compound, whose IR spectrum indicates the involvement of the carbonyl group in the declocalisation of the charge on the ylide carbanion: [31]



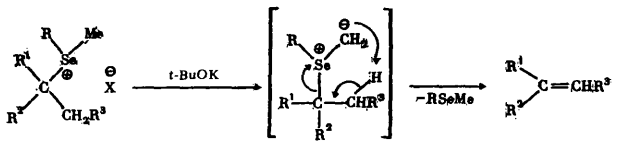
In the light or on slight heating, dimethylselenonium benzoylmethylide decomposes via a carbenoid mechanism with formation of *trans*-tribenzoylcyclopropane. [31] This reaction

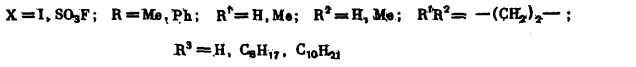
is a convenient method of synthesis of heteroaroylcyclopropanes:[36]



Unstabilised selenium ylides usually do not form carbenoid decomposition products. However, when benzylselenonium salts were treated with sodium amide, small amounts of *trans*-stilbene, which is formally a product of the dimerisation of phenylcarbene, were isolated.[37]

The reaction involving the intramolecular cleavage of unstabilised selenonium ylides is used to synthesise various olefins including sterically hindered olefins:[8]



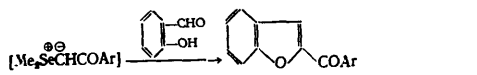


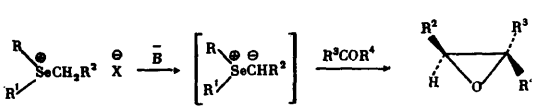
As a rule, unstabilised and monostabilised selenium ylides are not isolated but are used *in situ*, being generated from salts in the presence of the substrates with which the reaction is carried out.

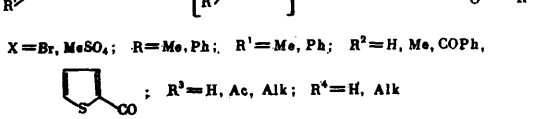
As carbenoid species, monostabilised selenium ylides are more nucleophilic than their sulphur analogues and they readily interact with electrophiles. The most convenient and productive method of carrying out the reactions of ketoselenonium ylides with electrophilic substrates involves the use of a two-phase system: chloroform–water with sodium hydroxide as the base. The ylide generated in the aqueous phase on treatment of the selenonium salt with alkali is immediately extracted chloroform. The salt which failed to react remains in the aqueous phase, which suppresses the secondary reaction of the ylide with the salt leading to a triarylcyclopropane.

The reactions of carbanions with electrophiles in a two-phase system are carried out[38] in the presence of a phase transfer catalyst. The reactions of selenium ylides do not as a rule require special catalysis.

The selenonium ylides stabilised with a phenylacyl[39] or cyclopentadienyl group[34] react with nitrosobenzene to form the corresponding nitrones. The reactions of selenium ylides with various carbonyl compounds lead to oxirans having the *trans*-confirguration[40–42] and the reactions with salicylaldehyde lead to 2-aroylbenzofurans:[41]

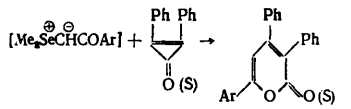


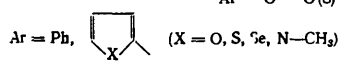




The interaction of selenonium ylides with activated multiple bonds usually begins as the Michael addition, the subsequent reactions of the betaines formed as a rule involving the elimination of the readily removed selenonium group as a result of intramolecular nucleophilic substitution.

A convenient preparative method of synthesis of trisubstituted α-pyrones and α-pyranthiones by the [3 + 3]dipolar cycloaddition of selenium monoketoylides to diphenylcyclopropenone or its thio-analogue has been developed:[32]

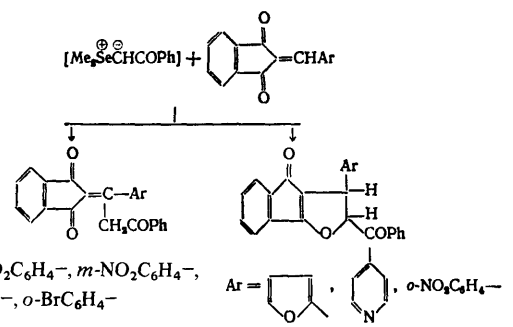




The reactions of cyclic selenium diketoylides, namely dimethylselenonium diketoylides formed from dimedone and indan-1,3-dione, with diphenylcyclopropenone can be used to synthesise condensed α- and γ-pyrones.[43]

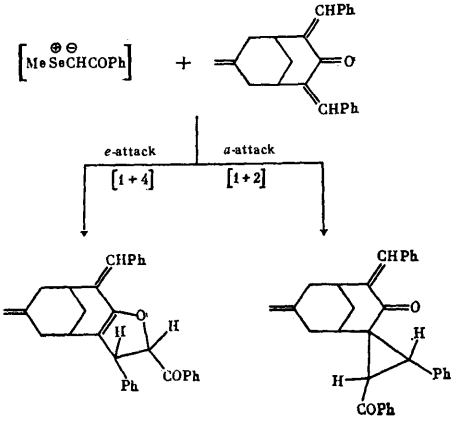
The interaction of selenium monoketoylides with activated acetylenes (dialkyl acetylenedicarboxylate or dibenzoylacetylene) leads to the formation of the corresponding trisubstituted furans.[44,45]

In contrast to sulphur ylides, the reactions of selenium monoketoylides with *para*-substituted 2-benzylideneindan-1,3-diones, having a conjugated bond system, begin with nucleophilic attack by the ylide carbon atom on the activated double bond. The betaine formed in this reaction splits off dimethyl selenide and, depending on the character of the substituent in the benzylidene group, either a 1,2-hydride shift takes place with formation of the Michael addition product or the dihydrofuran ring is formed. The reaction takes place stereoselectively and only the *cis*-isomers of dihydrofurans are formed:[46]



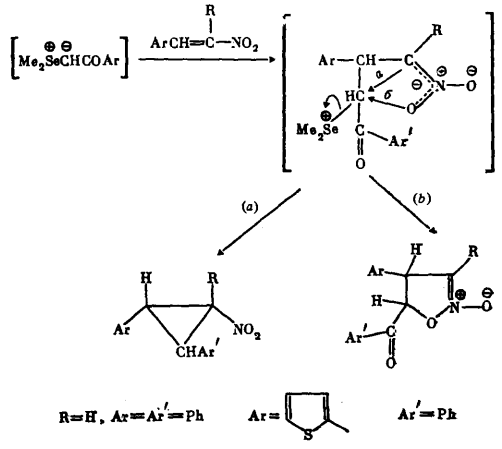
The reaction of selenium monoketoylide with dibenzylidene derivatives of a series of ketones (acyclic, cyclic, and bicyclic) in which both [1 + 2]- and [1 + 4]-cycloaddition is possible, have been investigated. It has been established that the interaction of selenium ylide with dibenzylidene derivatives of acetone, cyclopentanone, and cyclohexanone takes place as [1 + 2]cycloaddition to one of the double bonds of the dieonone with formation of two isomeric cyclopropyl ketones. In the case of the dibenzylidene derivative of bicyclo[3.3.1]ionan-3-one, the type of reaction, i.e. [1 + 2]- or [1 + 4]-cycloaddition, is determined by the direction of attack by the selenonium ylide (axial or equatorial). The attack by the ylide from the equatorial side relative to the given cyclohexane ring leads to the formation of the dihydrofuran ring as a consequence of the mutual approach of the carbonyl oxygen atom and the ylide carbon atom in the transition state. On the other hand, the attack from the axial side leads to the oxygen and ylide carbon atoms moving apart in the transition state and the formation of a three-membered ring becomes preferable. The reaction

takes place stereospecifically with formation of cyclopropane having the *cis*-configuration and of the *cis*-isomer of dihydrofuran:[47]

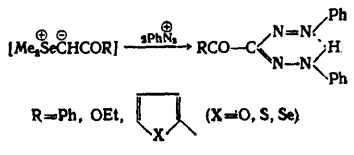


In all the cases investigated, the reaction involves only one benzylidene group.

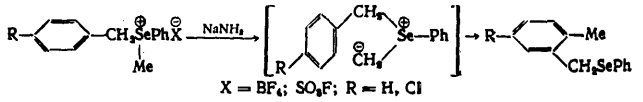
The conjugated nitro-olefins, in which there is a possibility of both [1 + 2]- and [1 + 4]-cycloaddition with formation of substituted cyclopropanes or isoxazoline *N*-oxides, constitute a convenient model for the study of reactions involving the cycloaddition of selenium ylides to an activated multiple bond. A necessary and sufficient condition for the occurrence of a reaction of the [1 + 4]-cycloaddition type is the presence of a substituent in the α-position relative to the nitro-group in the initial nitro-olefin. The nature of the substituent (alkyl, aryl, heteroaryl, or halogeno-) does not then influence the mode of reaction. The reaction takes place stereoselectively and is a convenient preparative method of synthesis of trisubstituted isoxazoline *N*-oxides in the *trans*-configuration:[48]



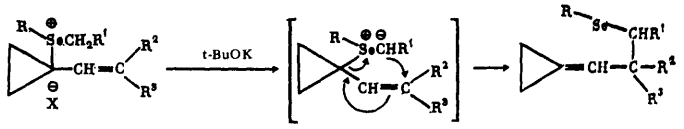
Among the electrophiles having the electrophilic centre at a heteroatom, detailed studies have been made of the interaction of selenonium acylmethylides with benzenediazonium chloride.[49] In contrast to phosphorus, nitrogen, and sulphur ylides, this reaction takes place with formation of 3-keto-1,5-diphenylformazans and constitutes a preparative method of their synthesis:



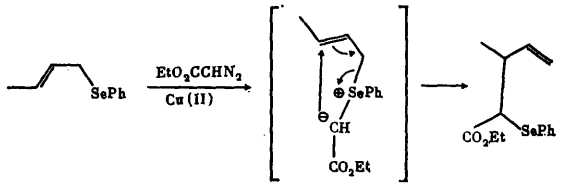
The [2,3]sigmatropic rearrangement of benzylselenonium ylides on treatment of the corresponding salts with sodium amide in liquid ammonia has been described:[37]



The [2,3]sigmatropic rearrangement of allylselenonium ylides is used to synthesise olefins:[9]



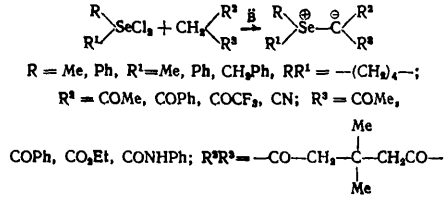
An analogous rearrangement has been observed on treating allyl selenide with diazoacetic ester in the presence of copper(II) sulphate:[33]



Thus unstabilised and monostabilised selenium ylides are convenient and very active reagents for the synthesis of various classes of organic compounds. Their ylide bond $\geq\bar{C}-\overset{+}{Se}<$ is weaker than the $\geq\bar{C}-\overset{+}{S}<$ bond in sulphonium ylides. R_2Se is a group which is more readily eliminated than R_2S. All the reactions with participation of selenonium ylides takes place under mild conditions. In terms of their behaviour, selenium ylides resemble nitrogen ylides more than sulphur ylides.

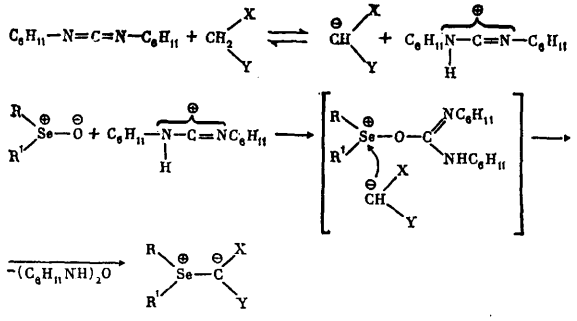
IV. DISTABILISED SELENIUM YLIDES

Distabilised selenium ylides have been obtained in satisfactory yields by condensing diorganoselenium dichlorides with compounds containing an active methylene group in the presence of a base (sodium ethoxide, potassium hydroxide, pyridine, alumina):[14,50–53]



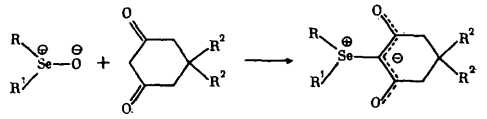
A general convenient preparative method of synthesis of distabilised selenium ylides involves the condensation of selenoxides with compounds containing an active methylene

group in the presence of dicyclohexylcarbodiimide: [16,51,52,54]



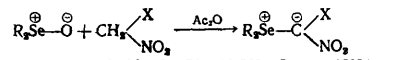
$R=R^1=Ph$; $R=Ph, R^1=PhCH_2$; $R=R^1=-(CH_2)_4-$, $X=Y=-CO-CH_2-C(Me)_2-CH_2-CO-$; $X=Y=COPh$; $X=COPh, Y=COCF_3$; $X=COCF_3, Y=CO$-(thienyl)

The asymmetric synthesis of a number of optically active selenonium diketoylides by the reaction of cyclic β-diketones with selenoxides in the presence of camphor-10α-sulphonic acid and anhydrous sodium sulphate has been achieved: [55]



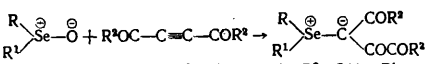
R = Ph, α-naphthyl, *o*-MeC_6H_4; 1,2,3-$Me_3C_6H_2$; R^1=Me, Ph; R^2=H, Me

Selenonium nitroylides have been obtained by this method: [19,56]



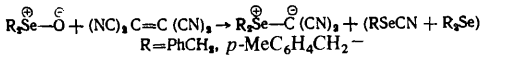
X = NO_2, CO_2Me, COPh; R=Ph, $PhCH_2$; $R_2=-(CH_2)_4-$

It is also known that selenoxides form selenium ylides by reaction with dimethylacetylenedicarboxylate [57,58] and dibenzoylacetylene: [59]



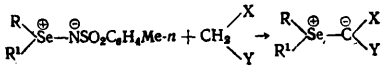
R=Me, R^1=Ph; R=R^1=$PhCH_2$, Ph; R^2=OMe, Ph

Selenium dicyanomethylides have been obtained by the reaction of selenoxides with tetracyanoethylene: [57]



R=$PhCH_2$, *p*-$MeC_6H_4CH_2-$

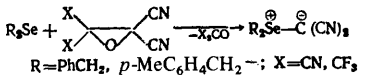
A method of synthesis of distabilised selenonium ylides from readily available selenimides and compounds with active methylene groups has been developed: [54]



R = R^1 = $PhCH_2$, Ph; $RR^1=-(CH_2)_4-$, X, Y=CN, COOMe, COMe, SO_2Ph

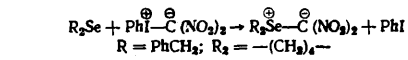
The rate of this reaction depends on the stability of the ylides formed.

Selenonium dicyanomethylides have been obtained by the reaction of selenides with activated oxirans: [57]



R=$PhCH_2$, *p*-$MeC_6H_4CH_2-$; X=CN, CF_3

Only one example of the synthesis of selenonium ylides from the ylides of other elements is known: [56]



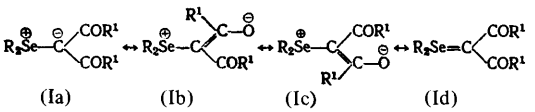
R = $PhCH_2$; $R_2=-(CH_2)_4-$

The yield of the ylides in this reaction depends on the nucleophilicity of the selenide used.

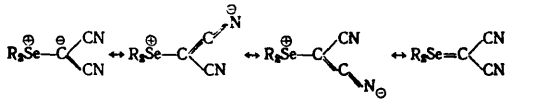
X-Ray diffraction data are available for only two distabilised selenium ylides: diphenylselenonium diacetylmethylide [56] and tetramethylselenonium dimedonylide. [60,61] These ylides have a trigonal pyramidal structure, at the apex of which the selenium atom is located.

Analysis of the bond lengths between the selenium atom and the ylide carbon atom and also of the bond lengths in the electronegative substituents indicates the involvement of electron-accepting groups in the declocalisation of the negative charge on the carbanion. [53,61] The IR. spectra of the distabilised selenonium ylides convincingly confirm this. [16,52]

The contribution of the dipolar resonance structures (Ib, c) and (IIb, c) to the ground state is extremely significant for selenonium diketo- and dicyanomethylides:



(Ia) (Ib) (Ic) (Id)

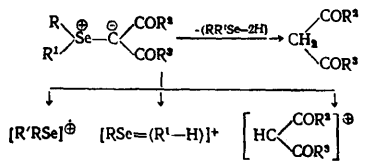


(IIa) (IIb) (IIc) (IId)

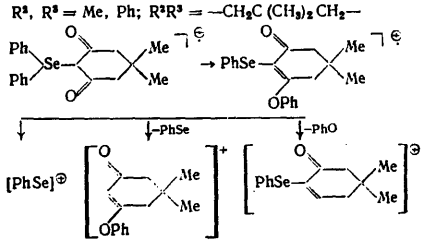
The selenium–ylide carbon bond lengths found in the distabilised selenium ylides [53,61] and also the ^{77}Se NMR data for these compounds [25] suggest a difinite contribution by the double bond character and the possibility of the formation of a $p_\pi-d_\pi$-bond using the selenium *d* orbital. [62] The contribution of the structures (Id) and (IId) in the selenium ylides is smaller than that of the analogous structures in sulphur ylides.

In aprotic solvents, the carbanionic fragment of selenonium ylides has the *W*-conformation, which has been confirmed by ^1H NMR and dipole moment data. [15]

On electron impact, selenium diketoylides decompose at the $\overset{+}{>}Se-\bar{C}<$ bond together with the migration to the anionic residue of the ylide of hydrogen or the group (in the case of diphenylselenonium dimedonylide) linked to the selenium atom: [63]



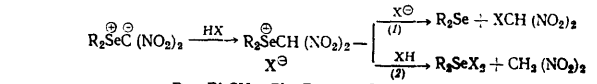
R = Ph; R^1 = Me, Ph; $RR^1=-(CH_2)_4-$; R^3, R^3 = Me, Ph; $R^2R^3=-CH_2C(CH_3)_2CH_2-$



With the exception of nitroylides, [19] the distabilised selenium ylides are extremely stable compounds resistant to the action of various nucleophiles: aqueous and alcoholic alkali, [51,52] amines, [50] and alkali metal alkoxides. [51] As a consequence of the delocalisation of the charge on the ylide carbon atom over two electron-accepting groups, their nucleophilicity is significantly lower than that of unstabilised and monostabilised selenium ylides. However, reactions with fairly powerful electrophiles and compounds containing activated multiple

bonds are characteristic of the distabilised selenium ylides; thus, they afford the corresponding hydrochlorides, which lose HCl near their melting points.

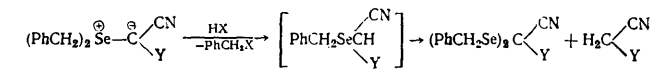
Selenonium dinitromethylides are protonated reversibly by inorganic acids containing weakly nucleophilic anions.[9] On treatment with acids having nucleophilic anions, the $\gtrless\overset{+}{S}e-\bar{C}\lessgtr$ bond dissociates. The intermediate salt is then capable of being cleaved at the $\gtrless\overset{+}{S}e-CH\lessgtr$ bond not only by the nucleophile counterion (pathway *1*) but also by the electrophilic molecule of the acid (pathway *2*):[19,56]



$R = RhCH_2$, Ph; $R_2 = -(CH_2)_4-$; X = Cl, Br

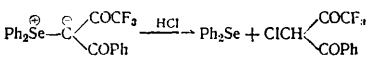
The preferred reaction pathway depends on the nucleophilic properties of the counterion; on passing from HCl to HBr, the contribution of pathway *1* increases.

Dibenzylselenonium dicyano- and cyanomethoxycarbonylmethylides are cleaved by acids only at the $\gtrless\overset{+}{S}e-CH_2Ph$ bond:[28]

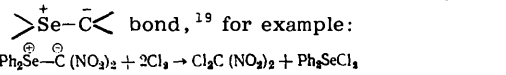


X = Cl, Br, NO_3, HSO_4, CF_3COO, $ClCH_2COO$; Y = COOMe, CN

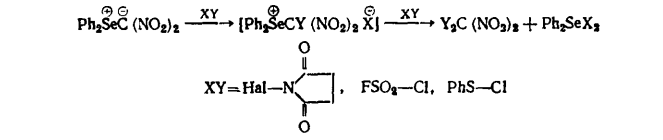
On the other hand, diphenylselenonium trifluoroacetylbenzoylmethylide is cleaved at the $\gtrless\overset{+}{S}e-\bar{C}\lessgtr$ bond on treatment with hydrogen chloride:[16]



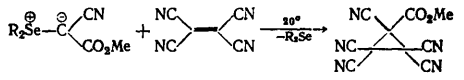
On interaction with powerful electrophiles (Cl_2, Br_2, SO_2Cl_2), diphenylselenonium nitroylides are also readily cleaved at the $\gtrless\overset{+}{S}e-\bar{C}\lessgtr$ bond,[19] for example:



Compounds with a "positive" halogen and benzeneulphenyl chloride also react with selenonium nitroylides under mild conditions, two "electrophilic" components of the reagent being joined to the carbanionic fragment, as in the interaction of distabilised ylides with acids:[19]

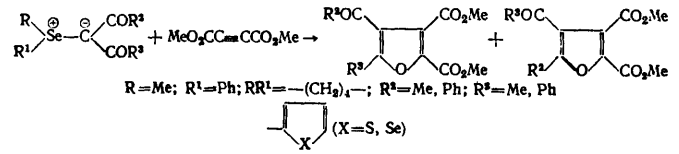


Distabilised selenonium ylides do not as a rule react with αβ-unsaturated ketones. However, substituted cyclopropanes have been obtained by the reaction of selenium cyanomethoxycarbonylmethylides with the highly electrophilic tetracyanoethylene:[57]

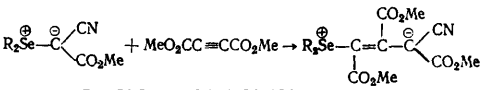


$R = PhCH_2$, p-$MeC_6H_4CH_2$.

The interaction of selenonium diketoylides with dimethyl acetylenedicarboxylate leads to tetrasubstituted furans:[50]

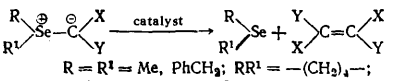


The reaction of selenium cyanomethoxycarbonylmethylides with dimethyl acetylenedicarboxylate results in the formation of only betaines, probably as a consequence of the reduced electrophilicity of the methoxycarbonyl group:[50,57]



$R = PhCH_2$, p-$MeC_6H_4CH_2$; $R_2 = -(CH_2)_4-$

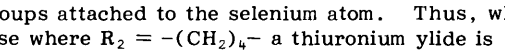
Distabilised selenium ylides readily decompose into the corresponding selenides and the products of the dimerisation of the carbanionic fragment on treatment with catalysts: tetramethylthioureas,[64] thioamides,[65] and episulphides:[66]



$R = R^1 = Me$, $PhCH_2$; $RR^1 = -(CH_2)_4-$;
X = CN, Y = CN, COOMe, COOEt

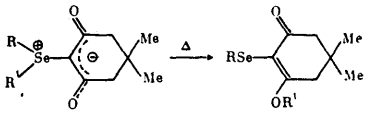
The mechanisms of all these reactions involve the initial attack on the thioderivatives by the ylides carbon atoms and the elimination of the selenide.[64-66]

Selenonium dinitromethylides are known to react with thiourea as follows:[56]



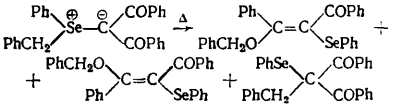
The course of the reaction depends greatly on the structure of the groups attached to the selenium atom. Thus, whereas in the case where $R_2 = -(CH_2)_4-$ a thiuronium ylide is formed in a high yield, when $R = PhCH_2$ the product is a 1:1 complex with thiourea, and in the case where R = Ph the reaction does not occur at all.

Under relatively mild conditions (refluxing in benzene or xylene), selenonium diketoylides rearrange with migration of the benzyl or phenyl group to the oxygen atom:[67]



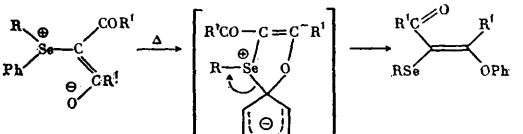
$R = PhCH_2$, Ph, Me; $R' = PhCH_2$, Ph

Only in the case of benzylphenylselenonium benzoylmethylide was the product of the Stevens rearrangement isolated together with that of the *O*-migration of the benzyl group:



The rearrangement of benzylphenylselenonium diketoylides apparently takes place stepwise via the formation of a radical pair and its subsequent recombination within a cage.

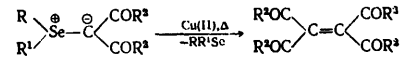
The migration of the phenyl group in methylphenyl- and diphenyl-selenonium diketoylides takes place via a mechanism involving intramolecular nucleophilic substitution in the benzene ring:[67]



R = Me, Ph; R^1 = Ph, $R'_2 = -CH_2-C(CH_3)_2-CH_2-$

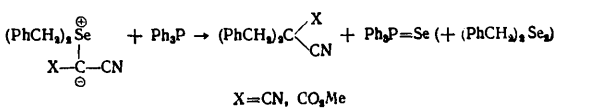
The capacity of the groups attached to the selenium atom for migration decreases in the sequence $PhCH_2$ > Ph > Me.[67]

Thermolysis of cyclic selenium diketoylides in the presence of copper(II) sulphate apparently proceeds via the formation of carbenes. As a result of the interaction with the initial ylide, the carbene is converted into the corresponding tetrasubstituted ethylene: [68]



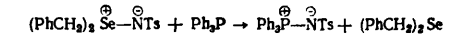
R, R^1=Me, Ph; R^2_2=—$CH_2C(CH_3)_2CH_2$—, *o*-C_6H_4—

The main pathway in the reaction of distabilised dibenzylselenonium ylides with triphenylphosphine involves the elimination of selenium with formation of triphenylphosphine selenide: [69,70]

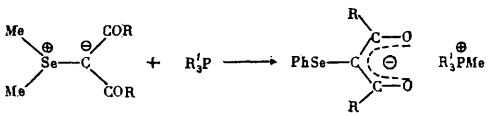


X=CN, CO_2Me

On the other hand, the reaction of dibenzylselenonium tosylimide proceeds with formation of triphenylphosphonium tosylimide: [70]

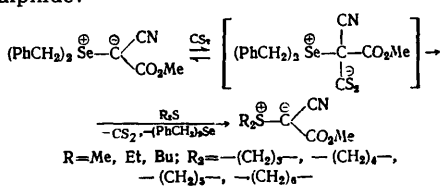


Triphenylphosphine and tris(dimethylamino)phosphine demethylate diketoylides with formation of phosphonium salts of enols: [71]



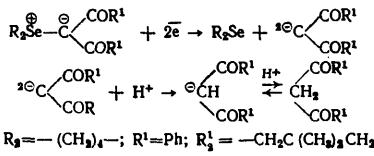
R=Ph, R_2=—$CH_2C(CH_3)_2CH_2$—, R^1=Ph, Me_2N

Dibenzylselenonium cyanomethoxycarbonylmethylide undergoes transylidation by dialkyl sulphides in the presence of carbon disulphide: [70]



R=Me, Et, Bu; R_2=—$(CH_2)_3$—, —$(CH_2)_4$—, —$(CH_2)_5$—, —$(CH_2)_6$—

In the polarographic reduction of stable selenium ylides at a dropping mercury electrode in dimethylformamide, the electrochemical cleavage of the carbon–selenium bond consists of two consecutive stages: [72]



R=Ph; R_2=—$(CH_2)_4$—; R^1=Ph; R^1_2=—$CH_2C(CH_3)_2CH_2$—

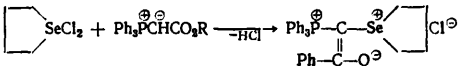
After electrolysis and treatment of the catholyte with water, dimedone and diphenyl selenide were detected in the reaction mixture. In the second stage, the dianions are apparently protonated with the initial formation of monoanions, which then combine with a proton and afford dibenzoylmthane and dimedone respectively.

V. BIS-ONIUM SELENIUM COMPOUNDS

The bis-onium compounds of selenium are ylide-salts and diylides containing, together with the selenonium fragment, onium fragments based on other heteroatoms (nitrogen, phosphorus, arsenic, selenium, and sulphur).

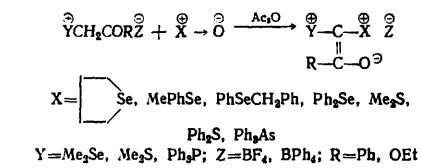
1. The Ylide-Salts of Selenium with Onium Groups at the Ylide Carbon Atom

The first attempt to synthesise ylide-salts containing the selenonium group involved the reaction of diorganoselenium dichlorides with alkoxycarbonylmethylenetriphenylphosphoranes. [73,74] Only in the case of selenolane dichloride, was the intermediate bis-salt resistant to the action of the nucleophilic chloride ion and a stable ylide-salt was obtained: [74]



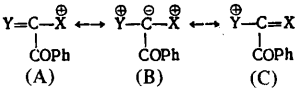
The reaction of diphenylselenium dichloride yields the corresponding α-chlorophosphorane and the reactions of the dichlorides of methylphenyl- and benzylphenylselenium involve the dealkylation of the intermediate bis-salt and the formation of α-phenylselenomethylenetriphenylphosphorane. [74]

A general preparative method of synthesis of selenium ylide-salts is the condensation of onium salts containing an active methylene group with diorganyl selenoxides, sulphoxides, and arsenoxides in the presence of acetic anhydride. The yield of the ylide-salts depends on the nucleophilicity of the initial oxide: [75–77]

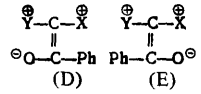


An essential condition for this reaction is the presence of sufficiently acid protons of the methylene group in the initial onium salt ($pK_a \approx 6–9$). [75] The phenyl groups attached to the onium atoms both in the initial salts and in the corresponding oxides give rise to steric hindrance to this interaction. [75,76] The high stability of the ylide-salts can be explained by the delocalisation of the negative charge on the carbanion over three centres: the two onium atoms and the carbonyl oxygen atom. This decreases the nucleophilicity of the ylide carbon atom. The ylide-salts are weaker nucleophiles than the acetate ion.

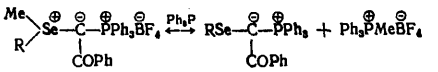
The structure of the cations of the phenylacylide-salts can be described by the set of mesomeric structures (A)–(C): [77]



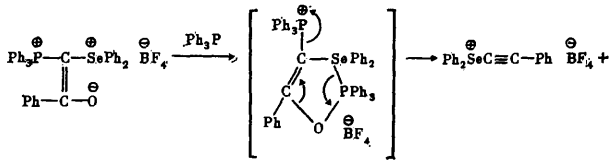
The onium groups of the phenylacylide-salts can be arranged in the following sequence in terms of their ability to stabilise the carbanion: $Ph_2S > Ph_3P > Ph_2Se > Ph_3As > Me_2S \approx$ MePhSe > Me_2Se. According to Ir and ^{1}H and ^{77}Se NMR spectra, [25,75–77] when the onium groups differ greatly (X = Me_2Se and Y = Ph_3P), the *trans*-structure (D) is formed with a considerable contribution by the structure (A), but, when the abilities of the onium groups to stabilise the carbanion are similar (X = Me_2S and Y = MePhSe), the ylide–salt consists of the *cis*- and *trans*-isomers (D) and (E).



The phenylacylide-salts containing the selenonium and triphenylphosphonium groups are demethylated on fusion with triphenylphosphine, forming Se-substituted phosphoranes: [78]

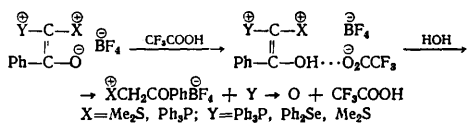


The ylide-salts without readily eliminated groups at the onium atom react differently. In this case, there is nucleophilic attack by triphenylphosphine on the selenium atom with subsequent elimination of triphenylphosphine and triphenylphosphine oxide and the formation of ethynylselenonium salts: [77]



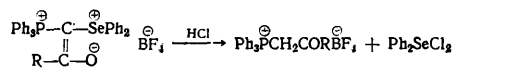
+ $Ph_3P{=}O$ + Ph_3P

Trifluoroacetic acid protonates phenylacylide-salts at the oxygen atom and the bis-salts obtained in this process are readily hydrolysed: [79]



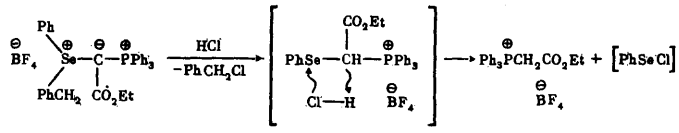
X=Me_2S, Ph_3P; Y=Ph_3P, Ph_2Se, Me_2S

The electrophilic cleavage of the phenylacylide-salts of selenium with hydrogen chloride [76,77] take place analogously to the corresponding reaction of dinitromethylselenonium salts: [56]



R=OEt, Ph

The interaction of benzylphenylselenonium ylide-salts with hydrogen chloride is accompanied by their dealkylation: [76]

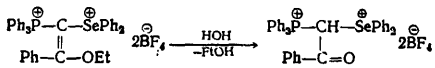


Selenonium phenylacylide-salts are alkylated at the oxygen atom [80] with formation of the (*E*)-isomer of the corresponding bis-salt with the *trans*-disposition of the triphenylphosphonium group or, in the absence of the latter, of the selenonium group, relative to the alkoxy-group:

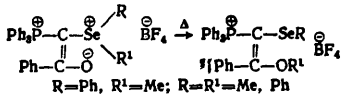


X=Me_2S, Y=Ph_2Se; X=Me_2Se, Y=Ph_3P;
X=Ph_2Se, Y=Ph_3P.

The bis-salts formed are readily hydrolysed by moist ether, for example: [80]

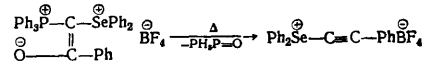


The thermolysis of selenonium phenylacylide-salts is accompanied by the migration of the methyl or phenyl group from the onium fragment to the oxygen atom as a result of the attack by the nucleophilic oxygen on the electrophilic carbon atom of the onium group. This results in the preferential formation of the (*E*)-isomer of the corresponding αβ-disubstituted triphenylstyrylphosphonium tetrafluoroborate with the *trans*-disposition of the triphenylphosphonium and alkoxy- or phenoxy-groups. The Stevens rearrangement has never been observed in such cases: [81]



R=Ph, R^1=Me; R=R^1=Me, Ph

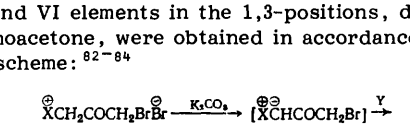
The intermolecular Wittig reaction with formation of ethynylselenonium tetrafluoroborate occurs in the rearrangement of a diphenylselenonium phenylacylide-salt: [77]



2. Selenium Ylide-Salts with Onium Groups in the 1,3-Positions

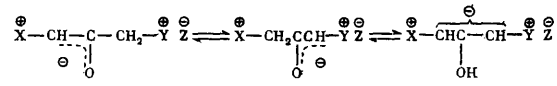
The presence in one molecule of an ylide-salt of two different onium groups in the 1,3-positions makes it possible to compare directly the degrees of their involvement in the stabilisation of the carbanion.

Ylide-salts containing two different onium centres with Group V and VI elements in the 1,3-positions, derived from 1,3-dibromoacetone, were obtained in accordance with the following scheme: [82-84]



X=Ph_3P, Py; Y=Me_2Se, MeS, Py, Ph_3As

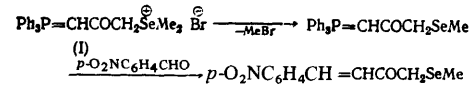
The existence of three tautomeric forms is theoretically possible for these salts: [83]



(A) (B) (C)

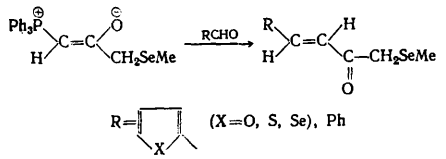
It was established from UV, IR, and ^1H, ^{31}P, ^{13}C, and ^{77}Se NMR data that the ylide-salt (I), containing together with the triphenylphosphonium group also the dimethylselenonium group (X = Ph_3P, Y = Me_2Se) exists in solution predominantly as the single tautomeric form (A) with an ylide phosphorane fragment. The ylide-salt containing the pyridinium and dimethylselenonium groups (X = Py, Y = Me_2Se) exists in solution in the form of an equilibrium between the two tautomeric forms (A) and (B) having the pyridinium ylide or salt fragment. The presence of the third form has not been detected. [25,82-84]

The ylide-salt (I) (ω-triphenylphosphoranylideneacetonyldimethylselenonium bromide) does not undergo the Wittig reaction, in contrast to the usual phosphorus ylides, as a consequence of the decrease in the nucleophilicity of the ylide carbanion under the influence of the selenonium group in close proximity. In the interaction with *p*-nitrobenzaldehyde, this ylide-salt forms a selenium-substituted αβ-unsaturated ketone. Under the influence of the nucleophilic bromide ion, the most electron-deficient $\gtrless$Se–Me bond is apparently cleaved under the reaction conditions and the resulting selenium-substituted phosphorane then enters into the Wittig reaction with *p*-nitrobenzaldehyde: [85]

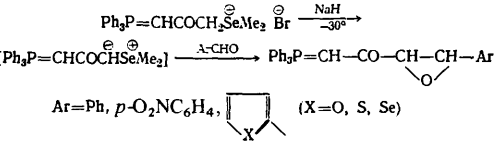


The ylide-salt (I) with selenonium and phosphonium groups in the 1,3-positions is readily demethylated by triethylamine with formation of methylselenoacetylmethylenetriphenylphosphorane which exists as the (*Z*)-conformer in $CHCl_3$: [84]

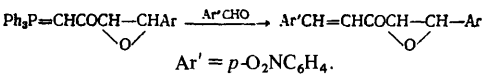
This phosphorane readily enters into the Wittig reaction not only with the reactive *p*-nitrobenzaldehyde but also with less reactive aromatic or heteroaromatic aldehydes, forming the corresponding αβ-unsaturated ketones having the *trans*-configuration and containing the Me–Se group: [84]



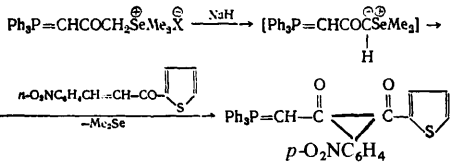
Bases such as sodium carbonate or hydroxide do not deprotonate the ylide-salt (I), although their basicity is sufficient for the formation of selenonium ketoylides from the corresponding selenonium salts. [31,32] When the ylide-salt (I) was treated with sodium hydride, a di-ylide was obtained *in situ* and its reactions with electrophiles—aromatic aldehydes and αβ-unsaturated ketones—were investigated. [82,85] Thus the reactions with aromatic aldehydes afford ketomethylenetriphenylphosphoranes containing the oxiran ring:



The selenonium ylide fragment in the di-ylide is more nucleophilic than in monoketoylides and reacts more readily with aromatic aldehydes. [82,85] The phosphorane formed under these conditions enters into the Wittig reaction under more severe conditions:



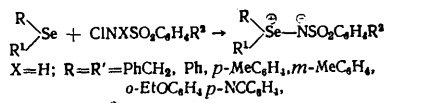
The C–P ylide bond remains unchanged in the reaction of the di-ylide with 2-(*p*-nitrophenyl)-1-(2-thenoyl)ethylene: [82,85]

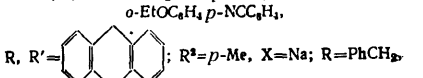


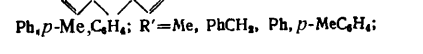
Thus, in the reactions with electrophiles, the selenurane and not the phosphorane fragment is more reactive in the di-ylide formed on deprotonation of the ylide-salt (I). The high reactivity of the di-ylides having this structure makes it possible to use them in organic synthesis, because, by selecting onium groups with different stabilising capacities and different reaction conditions, it is possible to achieve the selective interaction of a particular ylide fragment with electrophiles.

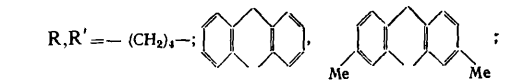
VI. SELENIMIDES

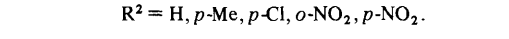
Selenimides have been synthesised by treating organic selenides with *N*-chlorosulphonamides or their sodium salts: [86–88]



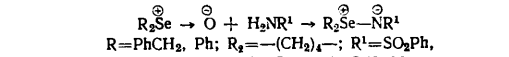








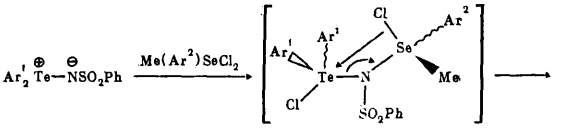
Selenimides are obtained in satisfactory yields by the condensation of selenoxides with sulphonamides and carboxylic acid amides: [51,88,90]

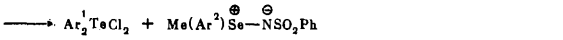


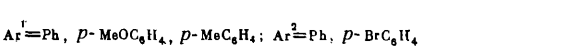
The occurrence of this reaction requires the presence of sufficiently strong electron-donating groups in the oxide and of electron-accepting groups in the amide. [90]

The reaction of *N*-(benzenesulphonyl)tellurimides with arylmethylselenium dichlorides affords *N*-benzenesulphonylselenimides and diaryltellurium dichlorides.

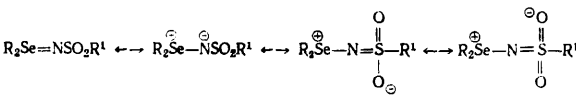
The possibility of such conversion of tellurimides into selenimides is due to the greater tendency of tellurium, compared with selenium, to form tetracoordinate compounds: [94]





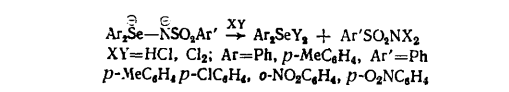


IR and UV-spectroscopic and ^{1}H NMR data indicate a dipolar structure of *N*-arenesulphonylselenimides with a considerable contribution to the ground state of the molecule by resonance structures with a positive charge on the selenium atom: [91]

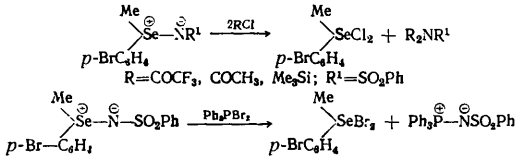


Selenimides with a chiral selenonium group have been synthesised. The pyramid of the onium selenium atom in selenimides has a high inversion barrier. [91]

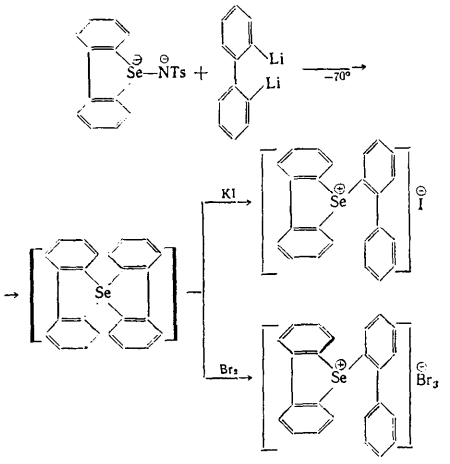
Measurements of the pK_a for selenimides have shown that their basicity is close to that of the anils of aromatic aldehydes. [91] Selenimides are stable compounds resistant to the action of aqueous alkalis and water at 20 °C. However, after prolonged heating with an aqueous 2 *N* solution of sodium hydroxide, they hydrolyse to selenoxides and arenesulphonamides. [87] Diaryl selenimides are readily cleaved by hydrogen chloride or chlorine at the $\overset{+}{\text{Se}}-\bar{\text{N}}$ bond: [87]



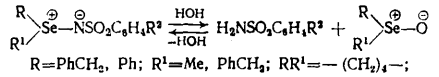
Selenimides react similarly also with acyl chlorides, triphenylphosphine dibromide, and chlorotrimethylsilane: [92]



solution of the latter with aqueous potassium iodide or bromine leads to its cleavage products: [86]

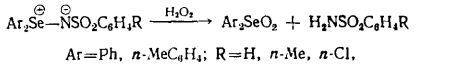


When aqueous solutions of selenides are heated, reversible hydrolysis takes place with formation of selenoxides and the corresponding amides: [87,88]



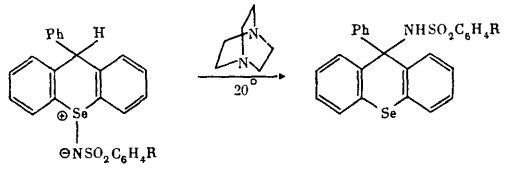
R=PhCH$_2$, Ph; R^1=Me, PhCH$_2$; RR^1=—(CH$_2$)$_4$—;
R^2=H, *n*-Cl; *o*-NO$_2$; *n*-NO$_2$

This reaction is accelerated in the presence of sodium hydroxide or silica gel. [87] Selenimides are oxidised by hydrogen peroxide or nitrogen dioxide and afford diarylselenones after subsequent treatment with water: [87]



Ar=Ph, *n*-MeC$_6$H$_4$; R=H, *n*-Me, *n*-Cl,
o-NO$_2$, *n*-NO$_2$

The reaction of *N*-arenesulphonylselenimides with 1,4-diazabicyclo[2.2.2]octane at 20 °C in benzene takes place quantitatively with formation of 9-arenesulphonamido-9-phenylselenoxanthenes, while hydrolysis on a silica gel plate (TLC) affords 9-phenylselenoxanthene 10-oxide: [93]



R=H; *n*-Me

Thus the data presented in this review show that in the last 15 years the chemistry of selenonium compounds has developed vigorously, particularly in recent years.

On the basis of selenonium compounds, in the first place the reactive and readily available selenium ylides, new preparative methods of synthesis have been developed for various classes of organic compounds: tertiary alcohols, olefins with different structures, including sterically hindered olefins, α-methylselenocarbonyl compounds, phosphoranes containing the methylseleno- or epoxy-group, heteroaroylcyclopropanes, nitrones, ketoformazans, oxirans, furans, condensed dihydrofurans, isoxazoline *N*-oxides, etc.

Various processes of the type of [1 + 2]-, [3 + 3]-. or [1 + 4]-dipolar cycloaddition with participation of selenium ylides, which in most cases proceed regioselectively and stereospecifically, are of special interest among the reactions of selenonium compounds.

All this shows that there are great prospects for the application of selenonium compounds in specific fine organic synthesis. One can undoubtedly expect the discovery of new reactions with participation of selenonium compounds, which will find practical applications. This will in its turn enhance the interest in the chemistry of selenonium compounds from the standpoint of their involvement in selective chemical processes.

The rapid development of the chemistry of organoselenium compounds is also indicated by the fact that, during the preparation of the manuscript of the review for publication, a monograph devoted to this topic appeared in the literature. [95]

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The Structure of Polymeric Colloid Particles and the Effect Associated with It

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The results of studies on the morphology and phase structure of polymeric colloid particles formed in the latex copolymerisation and seeded polymerisation of various monomeric compositions are surveyed. The role of the polar interactions at the interface and of the mobility of polymer molecules as factors influencing the location of the functional groups, the orientation of the macrochains, and the inversion of the polymer phases in the colloidal particles is discussed. The relation between the structure of the particles, on the one hand, and the colloidal behaviour of the system, the mechanism of film formation and the physical properties of the segregated polymers, on the other, is examined.
The bibliography includes 122 references.

CONTENTS

I. Introduction 174
II. The morphology of the particles of polymers with functional groups and its influence on the adsorption characteristics of the colloids, the polymerisation kinetics, and the structure of the films 175
III. The phase structure of composite particles and its relation with the morphology and properties of polymers and films 179
IV. Layer formation and phase inversion in composite particles and the properties of the "inverted" latexes and films 184

I. INTRODUCTION

Synthetic latexes in which the disperse phase consists of different chemical nature and the dispersion medium is water are typical polymeric colloids. Latexes are thermodynamically unstable hydrophobic colloids with a large interface characterised by different types of interfacial interactions. There has been a constant growth of interest in the industrial application of latexes. This is associated with the favourable factors in the technology of their manufacture and applications, the low cost of the petroleum raw material, and other familiar advantages of polymeric materials without organic solvents. The expansion of the range of latexes designed for different purposes is therefore one of the tasks in the chemistry and technology of polymers of current interest.

Vigorous studies have been carried out in recent years on the methods for the modification of latexes obtained from industrial monomers. One of the promising aspects of such research is the specific regulation of the internal structure of the colloidal particles of the polymer, without altering or altering only slightly its composition, and the determination of the relation between the structure of the particles, on the one hand, and the properties of the latexes and the polymers isolated from them, on the other.

Several reviews have been devoted to the morphological consideration of latexes consisting of heterogeneous particles. Latexes with the "core–shell" particle structure, used for the preparation of impact-resistant polymers,[1] and latexes with particles consisting of interpenetrating polymer networks, which are used to absorb sound and to extinguish vibrations,[2] have been examined. However, a systematic survey of the physicochemical characteristics of the formation of the structure of the polymer particles at their large interface with a polar medium is lacking in these reviews. This aspect of the research has become increasingly apparent in the studies carried out during the last 5–10 years, which have been partly described in a recent review.[3]

The morphology and structure of polymer particles with a diameter D_r = 50–500 nm are established during latex polymerisation where the macromolecules formed in them are fairly mobile because of the presence in the particles of the monomer, whose concentration is determined by the thermodynamic equilibrium conditions[4] and the monomer content in the reaction system.

The latex polymerisation begins with the generation of polymer-monomer particles (PMP) in the bulk of the aqueous phase. The possible regions where they are generated may be micelles made up of the emulsifying agent,[5,6] the molecular solution of the monomer in water,[7–9] and microdrops of the monomer.[10–12] This depends on the molecular solubility of the monomer in water, the ratio between this quantity and the colloidal solubility of the monomer in the emulsifying agent micelles, the types of the emulsifying agent and the initiator employed,[13] and the intensity of the hydrodynamic influence on the system.[14,15] With increase in the size of the PMP and depending on the chemical nature of the monomer, the recipe, and the way the process is carried out, various structural and physicochemical changes can occur in them: orientation of the macromolecules, separation and inversion of the phases, and the formation of transitional layers between them. Furthermore, the primary particles may undergo flocculation, heteroflocculation, and coalexcence. Changes of this kind lead to the formation of the final structure of the latex particles.

Attempts have been made at a theoretical consideration of the influence of the interface on the distribution and orientation of the macromolecules in the PMP.[16,17] Thus the idea of a gradient in the distribution of the density of the polymer in the bulk of the PMP, determined by the thermodynamic equilibrium conditions for the macromolecules in the particle, has been introduced.[16] On the basis of the concept of the increase in the free energy of restriction of the volume of the macromolecule between two surfaces in close proximity,[18] it has been assumed[16] that a uniform distribution of the macromolecules throughout the entire volume of the PMP is unlikely; they should migrate from the interface (which is assumed to be impermeable), where their conformational freedom and entropy are low, to the central region of the particle, where the macromolecules can assume the more favourable conformation of a statistical coil. Hence follows the model involving the ancapsulation of seed particles in the monomer after the attainment of the equilibrium degree of swelling.

A one-dimensional model of the distribution of the density of flexible long-chain molecules at an impermeable surface has been examined[19] as a function of the distance from the surface and of the energy of their attraction to the surface. It has been shown, that for an adsorption energy in excess of $0.693kT$, most of the segments of long-chain molecules are near the surface, while for a lower interaction energy, the density of their distribution is zero in this region. Evidently, for polar macromolecules or hydrophobic macromolecules containing hydrophilic units, the PMP–aqueous phase interface cannot be regarded as impermeable. For a freely jointed hydrophobic macromolecule containing a small fraction of hydrophilic units, the criterion of the entry of the latter into the aqueous phase has been determined theoretically.[17]

The polymerisation of polar monomers entails a limited flocculation of the PMP,[20–23] which is associated with the reduced energy of the adsorption of the emulsifier in such systems. The particles of the final latexes, consisting of aggregates of tens and hundreds of primary particles, are characterised by complex "grainy" structures. When they contain carboxy-groups, they decompose in an alkaline medium as a consequence of the ionised groups of the macromolecules and can be dispersed by vigorous stirring. This results in the formation of extremely highly dispersed polymeric colloids (D_r = 10–50 nm) with unique film-forming properties.[24,25]

The structure of the particles becomes much more complex on passing from latexes comprising homopolymers and copolymers to latexes made up of composite polymers, which were obtained by the successive polymerisation of individual monomers or their mixtures. In the heterogeneous particles formed, the chemical composition and topographic distribution of the individual polymers depend on their thermodynamic compatibility, the interaction with the aqueous phase, and the way in which the polymerisation is carried out. A change in the order of introduction of individual monomers into the reaction system influences significantly the chemical and physical structure of the resulting polymer and hence its macroscopic properties.[26] To be able to control the structure of the particles in order to obtain latexes and polymers with the necessary properties or in order to create in them regions with a specified reactivity, the introduction of individual monomers in stages during the synthesis has come to be used in industry.

This review is devoted to the morphology and phase structure of latex particles, the factors influencing them, and the effects associated with these factors. An attempt is made to give a systematic account of a wide variety of data which have accumulated in the scientific literature on these questions. In dealing with the physicochemical characteristics of the formation of colloidal particles and polymers, attention was concentrated on the role of the interfaces and molecular interactions at these interfaces in the heterogeneous system—latexes, particles, and films.

II. THE MORPHOLOGY OF THE PARTICLES WITH FUNCTIONAL GROUPS AND ITS INFLUENCE ON THE ADSORPTION CHARACTERISTICS OF THE COLLOIDS, THE POLYMERISATION KINETICS, AND THE STRUCTURE OF THE FILMS

1. The Morphology of Latex Particles and the Methods for its Investigation

Various physical, physicochemical, and chemical methods are used to investigate the morphology of particles. A universal method for the study of the shape, morphology, and phase structure of particles is electron microscopy (EM). The use of scanning EM made it possible to observe the structure of the surfaces of particles, especially those of immunolatexes.[27] The improvement of the preparatory technique in transmission EM (etching of the preparations and the use of specific reagents interacting with individual polymers) permitted the characterisation of the supermolecular organisation of the polymer and the identification of the topographical distribution of the individual polymers in the bulk of the particles. This possibility is due to the increase in the scattering of electrons as the polymer becomes more compact or when heavy metal atoms are introduced into it, which leads to a contrast effect.

In order to discover the supermolecular organisation of the polymer, the method involving the low-temperature etching of the specimens with active oxygen, obtained in an electrodeless high-frequency discharge, has been developed.[28] The less dense portions of the polymer are then rapidly destroyed, which makes it possible in many instances to discover the morphology of the polymer. Osmium tetroxide has come to be used widely as a specific reagent for polymers containing a carbon–carbon double bond.[29,30] Its introduction into the polymer increases the electron scattering[31] and leads to a greater contrast in particles whose composition includes a diene polymer. Preliminary treatment of the polymer particles containing carboxy- or ester groups with hydrazine hydrate or hydroxylamine, which interact with such groups, followed by increasing the contrast in the preparations with osmium tetroxide makes it possible to determine the topographical distribution of the polymer (for example, an acrylic polymer) in the bulk of the particles.[32]

In order to determine the content of poly(methyl acrylate) in the bulk of heterogeneous particles, the NMR method has been used: the content of this polymer in the solution obtained by the gradual hydrolysis of particles of polyacrylates with alkali was determined.[33] Methods involving the conductimetric and potentiometric titration of latexes with dilute solutions of alkali have been used to characterise the morphology of the particles of carboxylated polymers.[34] The concentration of the carboxy-groups located on the surface was determined from the characteristic points of inflexion in the titration curves. The fraction of the individual polymer in the surface region of the particles can be estimated by the adsorption titration of the latex with an emulsifier.[35] This method is based on the fact that the adsorption area of the molecule of the given emulsifier is a characteristic quantity for each individual polymer.[36,37]

Since the structure of the particles is preserved in the polymers isolated from the latexes,[26] it has been inferred in a number of studies from the properties of the latex polymers and films: from their spectroscopic,[8,38,40] mechanical,[41] relaxation,[42,47] and other physical characteristics. Thin-layer chromatography of the polymer solution in tetrahydrofuran on plates coated beforehand with silica gel has also been used to determine the phase structure of the composite particles of the poly(butyl acrylate)–polystyrene system (to determine the content of the grafted polymer).[48]

Previously it was regarded as self-evident (see, for example, Refs. 49–52) that the properties of particles are statistically uniform throughout the bulk and their behaviour in film formation is therefore determined mainly by the elasticity of the polymer. This idea was based, in particular, on electron microscope data for the surfaces of latex films, from which it followed that their structural element is the latex particle. However, it was shown later that, depending on its chemical nature and the character of its interaction with the aqueous phase, the polymer is organised in the particles in the form of some kind of supermolecular formation.[28,38] This is clearly demonstrated by the electron photomicrographs of the

particles and replicas from the surfaces of "etched" films[28] illustrated in Fig.1.[53]

The difference between the structures of the particles influences significantly the colloidal behaviour of the latexes[54,55] and the physical properties of the films.[41,56] This difference is manifested when the functional groups of different chemical nature are introduced into the given polymer by the copolymerisation method. It is significantly smoothed out after the reprecipitation of the latex films from an organic solvent, in which the initial structure of the polymer is altered.[56] The introduction of functional groups by homophase and not latex polymerisation has a much smaller influence on the physical properties of the polymer.[57]

2. Characteristic Features of the Copolymerisation in Colloidal Systems and the Morphology of the Particles Formed

One of the widely used methods for the modification of latex polymers involves the introduction of a small proportion of functional groups into their macromolecules by the copolymerisation method. The strengthening of the polymer and the improvement of its adhesion properties are achieved in this way and the ability to be cross-linked as well as other specific features are imparted to the polymer.

The copolymerisation in latex systems has its specific features distinguishing it from the homophase process, so that the structure and composite composition of the resulting macromolecules can differ significantly. Even in the copolymerisation of hydrophobic monomers, when the process takes place in a single phase (PMP), the effective copolymerisation constants depend on the interfacial resistance to mass transfer in the PMP of the monomers undergoing copolymerisation.[58] The diffusion-dependent limitations of the copolymerisation of the monomers in the PMP acquire special importance when the process is carried out under semicontinuous conditions providing for the gradual introduction of the monomer into the reaction system. Thus it has been shown for butyl acrylate and styrene that the effective copolymerisation constants and hence the structures of the macrochains differ as a function of the rate of introduction of the monomers.[59,60]

In the case of monomers whose solubilities in water differ appreciably, the copolymerisation reactions take place in several zones: in the aqueous solution, in the bulk of the particles, or on their surface. Depending on the contribution of each reaction, the effective copolymerisation constants differ to a greater or lesser extent from the constants in homogeneous processes. This has been demonstrated for the copolymerisation of methyl acrylate with methacrylic acid,[61] of chloroprene with methyl methacrylate,[62] and of methyl acrylate with vinyl acetate.[63]

The characteristic features of the structure of the macromolecules formed on copolymerisation in a colloidal system of a hydrophobic monomer with a small fraction of a hydrophilic monomer are significantly reflected in the morphology of the latex particles and polymers.

Theoretical examination of the behaviour at the oil–water interface of a one-dimensional freely jointed macromolecule consisting of hydrophobic units and a small proportion of hydrophilic units made it possible to define[17] the criterion governing the entry of the latter into the aqueous phase, which depends on the ratio of the potential energies of the two types of units in the oil and aqueous phases. This study permits the conclusion that, on formation of a flexible copolymer molecule at the interface between water and the hydrophobic monomer, copolymerising with a small proportion of a hydrophilic monomer, for a certain value of the partition coefficient of the latter between the phases, the hydrophilic units should emerge onto the surface of the PMP, influencing the conformation of the copolymer molecules. Thus, when the mobility of the macromolecules in the PMP is high, which is promoted by the presence of the monomer, a high polarisation temperature, and the flexibility of the polymer chains, the possibility arises of the assumption by them of an energetically most favourable conformation, which corresponds to the endeavour of the hydrophilic groups to emerge onto the interface with the aqueous phase.

So far numerour experimental data have accumulated, indicating the endeavour of the highly polar groups contained in the macromolecules to become concentrated on the surface of the particles, which is reflected in the colloidal behaviour of the latexes and in the physical properties of the polymers

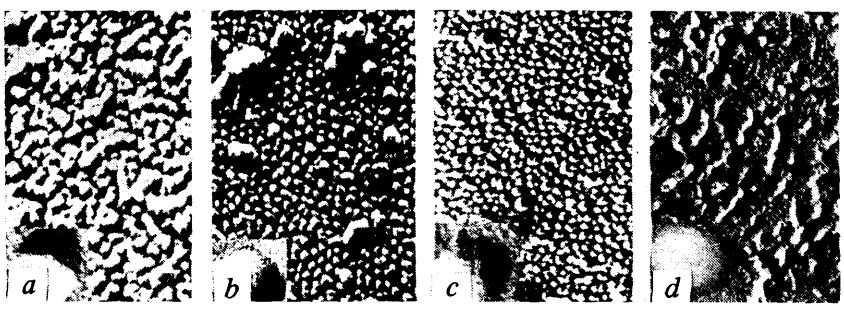


Figure 1. Electron photomicrographs of the replicas from the films: *a*) poly(alkyl acrylate); *b*) copolymer of alkyl acrylate with 3 mole% of methacrylic acid (MAA); *c*) copolymer of alkyl acrylate with 5 mole% of MAA; *d*) copolymer of alkyl acrylate with 5 mole% of the MAA amide after etching with oxygen. The electron photomicrographs of the initial latex particles are shown in the corners of the photomicrographs of the films.[53]

isolated from them.[64-66] The preparation of stable latexes in the absence of emulsifiers is based on this feature. Such latexes are formed when charged groups, forming part of the composition of the macromolecules (SO_4^-,[67-69] NR_3^+,[70] COO^- [71]) are concentrated on the surface, which occurs when the polymerisation is initiated by radical-ions or when a small proportion of an ionisable comonomer participates in the copolymerisation.

The concentration of the hydrophilic functional groups on the surface of the particles is greater the more hydrophilic the comonomer containing them. Thus, conductimetric and potentiometric titration studies of the distribution of the carboxy-groups of acrylic (AA) and methacrylic (MAA) acids in the particles of their copolymers with ethyl acrylate (EA) showed that in the case of AA the degree of concentration of these groups in the surface zone of the particles is higher than in the case of the more hydrophobic MAA, which diffuses more readily into the bulk of the particles.[34] In the copolymers of butadiene (Bd) with styrene (St), only some of the carboxy-groups of AA and MAA are distributed on the surface of the particles and for MAA their concentration in the bulk phase is higher.[72] The influence of the hydrophilicity of the unsaturated acid and its distribution in the particles has also been demonstrated in a study of the copolymerisation of St with itaconic, acrylic, and methacrylic acids: the first, most hydrophilic acid polymerised in the aqueous phase, the second is concentrated on the surface of the particles, and MAA, being most hydrophobic, is distributed in the bulk of the particles.[73]

3. The Influence of the Functional Groups of the Polymer on the Colloidal Properties of Latexes, the Polymerisation Kinetics, and the Structure of the Films

The localisation of the polar groups of the polymer on the surface of the particles hinders the adsorption of the emulsifier by the latter. This has been demonstrated in a study of the kinetics of the adsorption of sodium alkanesulphonate (by measurement of the electrical conductivity of the system) in the benzoyl peroxide-initiated polymerisation of butyl acrylate (BA) and its copolymerisation with 3 mole% of MAA, the amide of MAA, and *N*-hydroxymethylamide of MAA.[55]

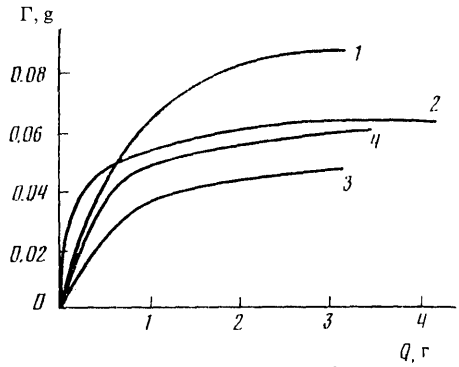


Figure 2. Dependence of the degree of adsorption Γ of sodium alkanesulphonate on the mass *Q* of the polymer formed in the polymerisation process: 1) BA; 2) BA–MAA (3 mole%); 3) BA–MAA amide (3 mole%); 4) BA–MAA *N*-hydroxymethylamide (3 mole %). Initial concentrations: 0.167 wt.% of sodium alkanesulphonate in the aqueous phase and 0.1 and 1 wt.% of benzoyl peroxide and t-dodecanethiol relative to the weights of the monomers respectively.[55]

The degree of adsorption of the emulsifier in the copolymerisation of BA with MAA amide is smaller approximately by a factor of two than in the homopolymerisation of BA (Fig.2). This has been explained by the mosaic structure of the surface of the copolymer particles, which is partly occupied by polar groups.[55] The mosaic structure of the particles of copolymers with unsaturated acids has been confirmed experimentally by the EM method, the carboxy-groups being labelled with uranyl acetate.[65] The presence of ionised carboxy-groups in the surface layer of the particles lowers the degree of adsorption of the emulsifier to a greater extent the higher the concentration of such groups. This has been demonstrated by the adsorption titration of the carboxyl-containing poly(ethyl acrylate) latexes with sodium dodecylbenzenesulphonate (at high pH).[66]

The localisation of the polar groups of the polymer on the surface of the particles also influences the polymerisation kinetics. This has been demonstrated by a dilatometric study of the polymerisation of BA and of its copolymerisation with 3 mole% of the MAA amide and *N*-hydroxymethyl amide.[55,64] Fig.3 shows that the copolymerisation is faster than the homopolymerisation. In view of the small fraction of the hydrophilic comonomer, the observed effect can be explained by the increasing hydrophilicity of the surface of the particles, which lowers the interfacial tension and hence increases the concentration of the monomer in the bulk of the PMP.[4]

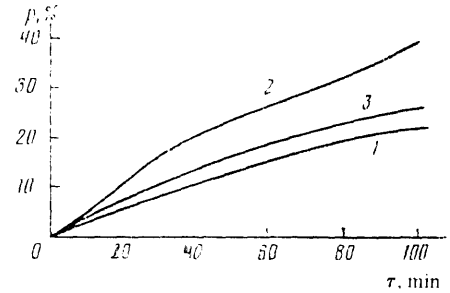


Figure 3. Variation of the degree of conversion *p* with time τ in the polymerisation process: 1) Ba; 2) BA–MAA amide (3 mole %); 3) BA–MAA *N*-hydroxymethylamide (3 mole %).[55] The polymerisation conditions are the same as in Fig.2.

When the surface of the particles is made hydrophilic by the introduction into the latter of highly polar groups, the resistance of latexes to aggregation in the cyclic freezing–thawing process increases,[61,74] and it becomes possible to synthesise colloidally stable latexes in the absence of an emulsifier.[75]

The localisation of polar functional groups on the surface of the particles (Fig.4*a*) promotes their interaction, both with one another and with the coreagent introduced into the aqueous phase, on contact between the particles in the film formation process. As a result, the structure of the film produced is a kind of globular network (Fig.4*b*). An advantage of this structure is an increase of the strength and thermal stability of the polymer. Thus films with a viscous flow temperature of 220 °C and a tensile strength of 60 kg cm^{-2} are formed on drying under room conditions from the latex of the copolymer of EA with 6.6 mole% of *N*-hydroxymethylmethacrylamide, which is capable of forming strong hydrogen bonds,[76] while the EA homopolymer exists in the viscofluid state even at room temperature [T_g = −20 °C].[40]

The study of the relaxation properties and dynamic characteristics of such films showed that they are strong three-dimensional networks, which do not break down on swelling in water at 75 °C.[41] Bearing in mind that chemical bonds are not formed between the hydroxymethylamide groups under the conditions indicated, the appearance of the network can be explained by the formation of hydrogen bonds between the "outer" groups coming into direct contact in the formation of the film. The structure formed under these conditions resembles that of a two-phase composite material: within the continuous phase, which is a network compacted by hydrogen bonds, consisting of the surface layers of colloidal particles and constituting a smaller proportion of the overall mass of the polymer, there are "cores", constituting a kind of filler, which are made up mainly of the linear polymer. The transition from a layer with a high degree of cross-linking to the linear polymer is continuous, so that one cannot speak of a true interface.

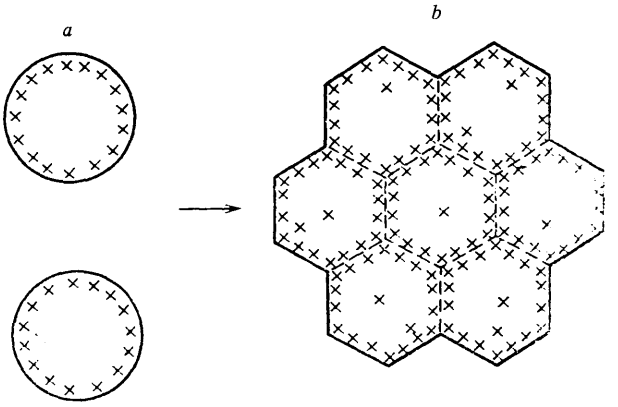


Figure 4. Schematic illustration of the structures of the particles (*a*) and films (*b*) of a hydrophobic latex polymer containing hydrophilic functional groups.

On deformation of composite materials of this kind, the mechanical properties of the continuous phase play a much more important role than would correspond to its volume fraction. Since, owing to the high density of the hydrogen bonds, the network has a high modulus of elasticity, the system as a whole also has a higher modulus of elasticity than the polymer with a uniform distribution of the same number of hydrogen bonds throughout its volume would have had. The chemical cross-linking process in such systems proceeds in an unusual manner: there is an optimum content of functional groups corresponding, as shown by approximate calculation, to the complete surface coverage by them for which the most complete cross-linking is achieved.[41]

In the latex copolymerisation of a hydrophobic monomer with another hydrophobic comonomer containing functional groups (glycidyl methacrylate, siloxanes), the latter are distributed statistically in the bulk and on the surface of the particles. Therefore, as a rule an increase in their concentration in the polymer induces a monotonic change in the degree of cross-linking, strength, and water resistance.[77]

Colloidal microgel particles approximately 10 nm in diameter, in which the reactive groups (double bonds) are present both within and on the surface of the particles, are of special interest. They are obtained by the polymerisation of divinyl monomers.[78,79] The cross-linking of the polymer in the copolymerisation process is apparently the cause of the small particle size in view of the insignificant swelling of the PMP in the monomer. Because of the small size of the colloidal particles, their reactivity is very high, since the functional groups, most of which are located on the large interface, are readily accessible to the coreagents.

4. The Morphology of the Particles and Films of a Polymer Containing Functional Groups Interacting Chemically with Water

The chemical interaction of the functional groups introduced into the polymer with water also leads to inhomogeneity of the composition of the particles. This is because the

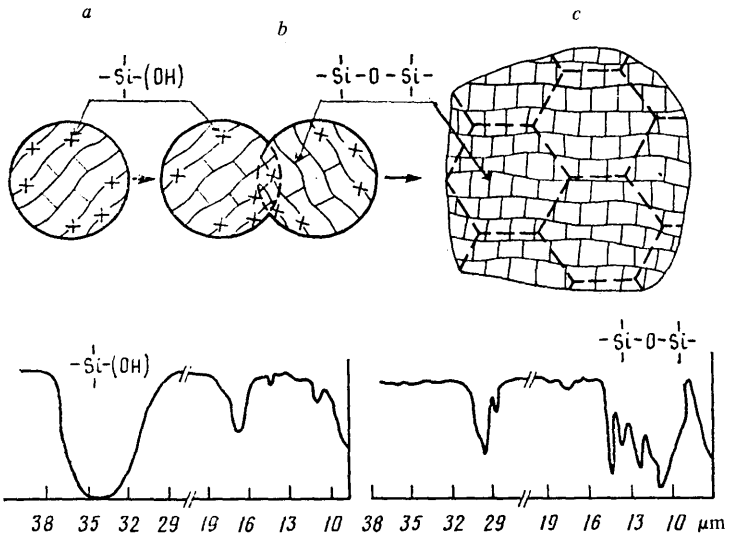


Figure 5. The mechanism of the formation of a film from the polymer latex incorporating siloxane: *a*) latex particles; *b*) coalescence of particles on drying of the latex; *c*) film structure. Above—schematic illustration of film formation; below—corresponding IR spectra.[82]

contribution and degree of the reaction of such groups, reacting on the surface of the particles, are greater than in the bulk phase. Thus the copolymerisation of acrylic and vinyl monomers with a small amount of siloxane leads to the formation of particles of the "core-shell" type, in which the structures of the polymer in the surface zone and in the bulk of the particles are different.[80-83]

This difference has been explained by the ability of alkoxysiloxanes to undergo hydrolysis and condensation reactions, whose relative contributions depend on the concentration of water in the reaction zone.[81,82] It has been shown by IR spectroscopy that, in the copolymerisation of vinyl chloride with vinylidene chloride and a small proportion of methacrylate-triethoxymethylsiloxane (0.2–0.8 mol%), the alkoxysilyl groups in the particles hydrolyse and undergo partial condensation; the latter apparently occurs in the nuclei of the particles, where the water concentration is minimal.[82] One may therefore assume that the copolymer particles consist of a nucleus comprising a polymer with a three-dimensional structure cross-linked by interchain $\geq$Si–O–Si$\leq$ bonds and of a shell made up of a linear polymer containing the hydroxysilyl $\geq$Si(OH) groups. Such morphology of the particles ensures their coalescence when the latex dries (latexes whose particles consist of only a cross-linked polymer with a three-dimensional structure are known not to form a strong film, because the coalescence of the particles is difficult). On further removal of water during the film formation process, the hydroxysilyl groups present in the film "matrix" condense with formation of oxygen bridges between the macromolecules and the polymer is thus cross-linked by chemical bonds throughout the bulk of the film. This process is illustrated schematically in Fig. 5. Film forming cold hardening latexes are obtained in accordance with this principle.

The presence of a small fraction of an alkoxysilane is appreciably reflected in the colloidal properties of the latex, inducing a decrease in particle size and this effect becomes more pronounced with increase in the concentration of the alkoxysilyl component. It may be that this is associated with the decrease in the monomer concentration in the partially cross-linked particle, which results in its growth, and also with the weakening of the particle coalescence process in cross-linked polymers.[81]

The data presented in this Section show that the interface in the vicinity of which the particles are formed plays a major role in the formation of their structure. The balance of the polar and dispersion interactions between the growing macromolecules and the aqueous phase determines the distribution of the functional groups on the surface or in the bulk of the particles. The localisation of the polar groups on the surface of the particles affects the polymerisation kinetics, the colloidal characteristics of the latexes, and the structure and properties of the films formed. Chemical interaction with water of the functional groups, distributed predominantly in the surface zone of the particle, leads to the inhomogeneity of the composition of the latter and affects the characteristic features of the mechanism of the formation from them of films having three-dimensional structures.

III. THE PHASE STRUCTURE OF COMPOSITE PARTICLES AND ITS RELATION WITH THE MORPHOLOGY AND PROPERTIES OF POLYMERS AND FILMS

Latexes with particles consisting of several polymers of different chemical nature† are used to impart particular properties to the composite materials isolated from them—impact strength, impermeability to sound, hardness, and low film formation temperature. They are obtained by two- or multi-stage polymerisation: the "seed" latex is synthesised initially and then the second, and if necessary, the third etc. monomers are polymerised in its presence. Depending on the method used to carry out the second and subsequent stages, the composite particles are formed in each seed particle, or as a result of the heteroflocculation of the new particles with the seed particles, or by a combination of both processes.

The polymers isolated from latexes with composite particles consist of a matrix in which the second polymer is dispersed. It is linked to the matrix by chemical bonds or by transitional layers of intermediate composition or solely via the physical interpenetration of the polymer chains. The physical state of the two phases depends on the purpose of the material: in impact resistant plates there is a vitreous matrix and an elastic nucleus, in film forming latexes, there is a rigid nucleus and an elastic matrix, and vibration damping systems are obtained from latexes having particles which consist of interpenetrating networks of two polymers. In general, the morphology of such materials is determined by many factors—the structure of the units of the macromolecules, their steric structure, the size and disposition of individual domains, etc. The possible combination of factors can be extremely varied and can depend on the choice of the monomers and the polymerisation method.

1. The Mechanisms of the Formation of the Phase Structure of the Particles of Composite Polymers

From the standpoint of the topochemistry of polymerisation, the phase structure of particles consisting of two polymers (1 and 2) is formed to a first approximation either on polymerisation of the monomer (monomers) 2 within the seed particles of the polymer 1 or as a result of the heteroflocculation of the seed particles of the polymer 1 with the new particles of the polymer 2 formed outside them. In the former case, the polymerisation is carried out after the seed particles have been swollen in the monomer 2 and the attainment of a thermodynamic equilibrium distribution of this monomer in PMP is very important for the formation of the phase structure of the particles. The formation of the particles via the second mechanism is characteristic of semicontinuous conditions in the polymerisation of monomers appreciably soluble in water and is not associated with the attainment of the equilibrium swelling of the seed particles in the monomer 2, depending significantly on the content of the emulsifier in the system.

(a) *Polymerisation in the bulk of the seed particles swollen in the monomer.* Seeded polymerisation, which is used to produce most of the impact resistant polymers (ABS-plastics), is carried out in two stages: initially a latex of the elastomer 1—butadiene (Bd) or the Bd–St copolymer—is obtained and then one polymerises in its presence the monomers 2—acrylonitrile (ACN) and St—absorbed by the seed particles 1.[84] In the second stage, the polymerisation takes place in the swollen particles. It has been suggested that the growing polymeric ACN–St radicals are grafted to the double bonds of the elastomer and the grafted polymer layer strengthens both polymer phases. The particles of such latexes are characterised by a complex morphology: a concentric shell of the polymer 2 is formed on the surface of the seed particles of the polymer 1; the polymer 2 is incorporated in the form of inclusions also in the nuclei of the composite particles produced.[84]

†Below, such particles will be referred to as composite.

There exist different views on the mechanism of the formation of the structure of composite particles of the "core-shell" type. The commonest view is that the polymers 1 and 2 are imcompatible[85,86] or that the solubility of the polymer 1 in the monomer 2 is limited.[87] However, it has been shown experimentally that such a structure is formed also for completely compatible polymers, namely in the seeded polymerisation of St containing a small amount of Bd[16] or of tritiated St[88] on a styrene latex after the attainment of thermodynamic equilibrium swelling of its particles in the monomer. The polymer formed in the second stage was identified in the former case by labelling Bd with osmium tetroxide and in the latter case the autoradiographic method was used. The morphology of the particles formed in this process can be seen from the electron photomicrograph in Fig. 6.[88]

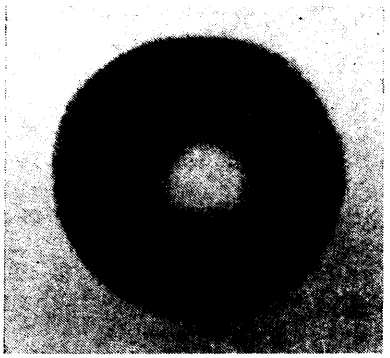


Figure 6. Electron photomicrograph of a section through a latex particle obtained as a result of the St–Bd (0.7%) seeded polymerisation on a polystyrene latex.[88]

In order to explain the result, the authors put forward the hypothesis that the distribution of the monomer in the PMP obeys the laws of microthermodynamics and not macrothermodynamics. Theoretical estimation of the influence of the particle–water interface on the thermodynamics of the dissolution of the polymer in the colloidal particles on the assumption that the macromolecule is attached via one end to an impermeable and inert surface[18,19] led to the conclusion that, in the thermodynamic equilibrium swelling of the polymer in the solvent, segments of the macromolecule tend to be repelled from the surface, leaving an excess of the solvent near it. Since the macromolecules in a latex particle are attached via the terminal SO_4^- group to the surface of the particles,[89] the majority of the segments of the polymer 1 in its particle subjected to equilibrium swelling in the monomer 2 are localised in the central region and the monomer 2 tends to be concentrated in the peripheral zone, as a result of which a gradient of its concentration is established in the bulk of the particles. The polymerisation of the monomer 2 therefore takes place preferentially in the peripheral zone of the particles, which in fact leads to the formation of the "core–shell" structure even when the monomers 1 and 2 are completely miscible.

The idea of a monomer concentration gradient in the particle which has undergone equilibrium swelling conflicts with the classical theory of latex polymerisation, which postulates a uniform distribution of the monomer in the PMP.[85] However, it is believed[16] that the experimental data on the kinetics of the polymerisation of St (the duration of the constant rate period, the rate, and the number of radicals per particle) agree with the main postulates of the theory[90] if the treatment is based on the corresponding model. The morphology of the PSt particles (Fig. 6) is difficult to explain from the standpoint of a uniform distribution of the monomer in the PMP. In the latter case, it was necessary to assume the presence of forces which promote the diffusion of the macromolecules, formed in the second stage, towards the periphery of the particles. Such a phenomenon could occur under conditions where there is a considerable difference between the polarity of the monomers formed in the two stages (see below), which is ruled out in the case under consideration. For a uniform distribution, one would have to expect the appearance of a "cellular" structure of the type of inclusions of one polymer in the other. The appearance of inclusions when the polymers 1 and 2 are incompatible may be a consequence of the entry of the radical of the monomer 2 into the seed particles of the polymer 1, the radical serving as the centre for the independent polymerisation of the monomer localised in a medium with a high viscosity.[91]

The formation of inclusions can lead to the formation of non-spherical particles, which has been observed in the seeded polymerisation of St on a butadiene–styrene latex and of a mixture of vinyltoluene with Bd on a styrene latex.[91] The formation of inclusions in composite latex particles is indicated by the results of a number of studies[45–47] in which the structure of the polymers isolated from latexes obtained by the seeded polymerisation of various monomers, namely vinyl acetate, alkyl acrylates and methacrylates, and MAC, was investigated by relaxation methods.

In the non-equilibrium swelling of the seed particles in the second monomer, this restriction of the diffusion of the latter into the particles during the polymerisation can itself be the cause of the formation of the "core–shell" structure. For example, in the polymerisation of St, which is usually carried out at 65–70 °C where the seed particles are in a vitreous state, the process in the bulk of the particles is retarded and may cease altogether as a result of the limitation of the diffusion of the monomer—it migrates into the shell of the particle.[92] On raising the temperature to 90 °C, the polymerisation shifts into the bulk of the particles.[93] This difference is reflected both in the process kinetics and in the structure of the particles formed.

When the monomer 2 is introduced gradually into the seed latex of the polymer 1 (semicontinuous polymerisation conditions), the preferred zone in which the process takes place becomes the shell of the seed particle enriched in the monomer.[94]

The conversion of the monomer in the seed latex should be important both for the polymerisation of the second monomer and for the phase structure of the particles of the final latex. Thus, when the polymerisation of alkyl acrylates and polystyrene particles compared after 100 and 80% conversion of St, it was shown that in the latter case the process is faster and the shell enriched in the alkyl acrylate is bound more strongly to the cores of the composite particles.[95] These effects can be explained by the fact that, when the conversion is incomplete, the polymerisation of alkyl acrylate or its copolymerisation with St proceed from the very beginning in the viscous medium of the swollen PMP (gel effect) and that a fairly thick transitional layer of the copolymer arises between the two polymers. The presence of a transitional layer of a grafted or statistical copolymer in the composite particle, between the nucleus and the shell, is very important for the strength of the combination of the segregated polymers 1 and 2.

In the seeded polymerisation of St on the poly(butyl acrylate) latex, the amount of grafted polystyrene depends on the method used to introduce St. The monomer can be introduced in three different ways: after the preliminary equilibrium swelling of the seed particles in it, all at once, or gradually at a constant rate. The grafting takes place in all cases but it attains the maximum extent (25%) when St is introduced at once, this being followed by the values obtained in equilibrium swelling (16%) and under the conditions of the gradual introduction of the monomer (7.7%).[48] This difference has been attributed[48] to the different mobilities of the molecules of the monomer absorbed by the seed particles: when St is introduced gradually, its degree of absorption is lowest, which reduces the mobility of the molecules and the degree of grafting, while in the other two cases the above parameters are correspondingly greater. Under the conditions of a low degree of grafting, the appearance of "dumb-bell-shaped" particles was observed during the storage of the latex and was explained by phase separation. Such particles were not formed when the degree of grafting was increased. All the latexes obtained by seed polymerisation afforded on drying transparent films, while the films obtained in a mixture of homopolymer latexes readily cracked and became turbid. This indicates the important role of the transition layer (grafted copolymer) between the imcompatible polymers in the film formation process.

In particular, systems used as vibration damping polymers are obtained by seeded polymerisation.[96] Interpenetrating polymer networks (IPN), obtained by the polymerisation of a monomer containing a cross-linking agent located within the particles of the seed latex of the cross-linked polymer swollen in the cross-linking agent, permit the attainment of this effect. The cross-linking agents are bimonomers of the type of dimethacrylate-ethylene glycol, divinylbenzene, etc., which are used in small amounts (~0.4%), so that excess cross-linking should not prevent the moulding and fusion of the composite material isolated from it.

The degree of phase separation and the size of the phase domains in such systems are limited by the compatibility of the polymers and by the degree of cross-linking and are controlled by the chosen composition of the reaction mixture. Even when polymers with similar solubility parameters are obtained jointly, the individual domains can consist of different polymers and may make their individual contributions to the properties of the composite material, influencing its operation characteristics. Thus a relation has been established between the composition of structured acrylate-methacrylate polymers obtained in the first (ethyl methacrylate–EA copolymer) and second (BA–EA copolymer) polymerisation stages, on the one hand, and the width of the temperature range of the effective attenuation of sound, on the other.[97]

The study of the dynamic characteristics of composite materials of the type of IPN in the temperature range from −110° to 170 °C shows clearly that they depend not only on the nature of the polymers but also on the phase structure and morphology of the particles.[98]

In the systems examined, the initial latex particle contains two cross-linked polymers, and systems in the particles of which only one of the grafted polymers is cross-linked are also classified as IPN.[99] They can be obtained, for example, by the seeded polymerisation of MMA on the latex of the MMA–1,3-butylene dimethacrylate copolymer.

Systems of this type have been obtained to increase the impact strength of poly(vinyl chloride) obtained by emulsion polymerisation.[100] In the polymerisation of the St–MMA mixture on seed latexes of the Bd–St and BA–ethylene glycol dimethacrylate copolymers with particle diameters in the range 50–200, a structure of the "core–shell" type is formed regardless of the solubility parameters. The character of the shell arising from the very beginning of the process depends on the degree of adsorption saturation of the surface of the seed particles by the emulsifier, i.e. on the emulsifier concentration in the system. For a low degree of saturation (under 25%), an upper layer of non-uniform thickness is formed; for a high degree of saturation, the shell is formed as individual surface growths and a new fraction of particles is produced. In order to form a concentric shell, it is necessary to achieve the optimum degree of adsorption saturation on the surface of the particles for which the maximum degree of grafting is believed to be achieved.[100]

(b) *Polymerisation with formation of new particles.* In the seeded polymerisation of St on the polystyrene latex, new particles may appear, which, depending on the emulsifier concentration, can flocculate with the seed particles or can be retained as an individual fraction.[101] In the two-stage seeded polymerisation of the BA–MAA mixture, the formation of new particles was observed when the monomers and the emulsifier were gradually introduced into the reaction system. As these particles appear, they flocculate with the seed particles of poly(methyl acrylate) (PMA)[43] or PSt[44] in such a way that the total number of particles hardly changes (Fig.7). Flocculation takes place because the newly formed monomer-enriched particles are less stable than the seed particles.

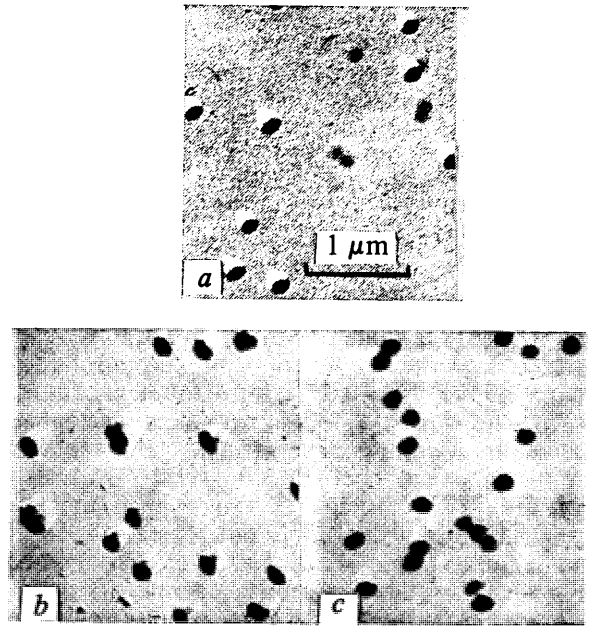


Figure 7. Electron photomicrographs of the particles formed in the BA–MAA seed polymerisation on a PMA latex with gradual introduction of the monomers: *a*) seed latex; *b*) second stage; *c*) final latex.[43]

This results in the formation of composite particles consisting of the polymers obtained in the first and second stages, which are located in the core and in the peripheral zone respectively. A study by the dielectric relaxation method of the PMA–P(BA–MAA) polymers isolated from the latex[43] showed that the particles produced consist mainly of two segregated polymers, PMA and P(BA–MAA), and a small

fraction of a copolymer having the intermediate composition P(MA–BA–MAA), which is apparently located at the interface between the segregated polymers. This copolymer, which plays the role of a transitional layer, might have been produced at the beginning of the second stage as a result of the copolymerisation of the second monomer with the residual monomer of the seed latex.

2. The Influence of the Compatibility of the Polymers and the Phase Structure of the Composite Particles on the Properties of Polymers and Films

The influence of compatibility on the properties of composite latex polymers and films has been investigated in binary systems with satisfactory (PMA–PVA), limited (PMA–PMMA), and poor (PMA–PSt) compatibility.[26] The systems were obtained by mixing the homopolymer latexes, by the joint polymerisation of a pair of monomers, and by seed polymerisation, which was carried out after the equilibrium swelling of the seed latex in the second monomer.

The study of the temperature dependence of the modulus of shear of the specimens showed that the presence of a more rigid component does not have an appreciable effect on the T_g of polymers with limited compatibility within a wide concentration range. Thus $T_g \cong 4°$, which is close to T_g for PMA, has been found for the PMA–PMMA composition with component ratios (by weight) from 75:25 to 50:50, obtained either from a mixture of homopolymer latexes or by seeded polymerisation. The value $T_g \cong 15°$ was found for the statistical MA–MMA copolymer having the composition (by weight) 75:25, which is in good agreement with the calculated value.

Hence, it has been concluded that the composite materials obtained contain fairly large regions of segregated polymers and that the latex particles retain their individuality in the isolated polymers and films.[26] This has been confirmed by data obtained for the fully compatible PMA–PVA polymers: for the ratio 50:50 by weight, two regions were observed in which there was a marked change in the modulus of shear—at 6 °C, which is close to T_g for MA, and at 32°, which corresponds to T_g for PVA. In the seeded polymerisation of the incompatible polymers investigated, grafting occurred, which ensured the formation of a transparent film from the latex at room temperature. The copolymer latexes obtained under these conditions did not exhibit a film forming capacity and mixing of the homopolymer latexes resulted in the formation of cloudy films. The latter demonstrates yet again that the transitional copolymer layer between the segregated incompatible polymers in the particles is very important for the film formation process. Such a layer affects also the strength of the polymer. Thus it has been established that the presence of a small fraction (several per cent) of the grafted ethylene–styrene copolymer in the polyethylene–polystyrene incompatible polymer mixture greatly increases the strength of the composite material.[102]

Data concerning the fomation of films from latexes with composite particles of rigid incompatible polymers are of interest. Such latexes with two-layer monodisperse particles have been synthesised by the emulsifier-free seeded polymerisation of St on a PMMA latex.[103] The films, obtained by fusing the particles, were distinguished by a high mechanical strength and transparency provided that the particle diameter did not exceed 200 nm. With increase in particle size (D_r > 300 nm), the fused films become appreciably cloudy. This can apparently be accounted for by the formation on fusion of smaller particles of the PSt–PMMA diffusion layer between the phases, whose thickness is comparable to the particle diameter; with increase in the relative volume of the incompatible polymer phases, the influence of the transitional layer diminishes.

The mechanical properties of the PMMA–PEA films (D_r = 290–370 nm), obtained by drying, under normal conditions, latexes with two-layer particles comprising vitreous and elastic polymers with limited compatibility, as well as the minimum film formation temperature (MFT) depend on the ratio of the polymers and on the morphology of the particles.[104] Fig. 8 shows that, for the same MMA content in the polymer (about 50%), the MFT for the copolymer latex is 30 °C, while the corresponding temperatures for the latexes obtained by the seeded polymerisation of MMA on PEA and of EA on MMA are respectively about 70° and 0 °C depending on which of the polymers—vitreous or elastic—constitutes the film matrix. Similarly the modulus of elasticity corresponding to 100% extension of certain films made from latexes with particles having a two-layer structure exceeds by a factor of 4 the modulus of the copolymer film. The data obtained show that the film forming properties of the latexes are affected not only by the structure of the polymer (composite polymer, copolymer) but also by the order in the distribution in the bulk phase of the particles of the segrated polymers. This order can change as the films age during the attainment of thermodynamic equilibrium.[105]

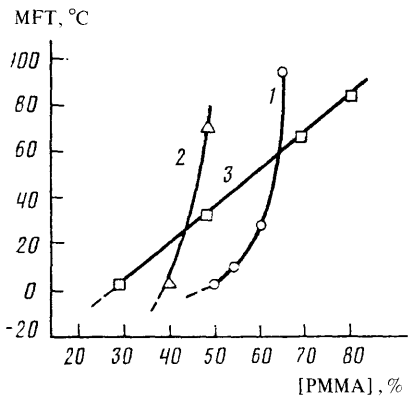


Figure 8. Dependence of the MFT for the latex on the particle structure: 1) PMMA in the core and PEA in the shell; 2) PEA in the core and PMMA in the shell; 3) statistical EA–MMA copolymer.[104]

The marked dependence of the film forming and mechanical properties of the films on the structure of the particles has been observed for latexes obtained by the semicontinuous polymerisation of the MA–BA–MAA, MMA–BA–MAA, and St–BA–MAA compositions.[42,44] The tensile strength and its change after the prolonged storage of the latex films obtained by seeded polymerisation differ significantly from the analogous characteristics of statistical copolymer dilms and latex films formed from mixtures of latexes of the corresponding polymers, as can be seen from Fig. 9. In order to elucidate the causes of this difference, a study has been made of the structure of the films by the dielectric and spin–lattice relaxation methods.[42]

As an example, Fig. 10 presents the temperature variation of the tangent of the dielectric loss angle (tan δ) at different frequencies for MMA–BA–MAA (50:45:5) polymer films obtained both from a mixture of latexes (curve 1) and from a

latex of the same polymers synthesised by seeded polymerisation (curves *2*, *2'*, *2''*, and *2'''*). At a frequency of 1 kHz, the range of tan δ_{max} for the film consisting of the mixture of latexes is entirely symmetrical (curve *1*). The temperature variation of tan δ for the specimen consisting of the latex obtained by seeded polymerisation (curve *2*) is of a different character: the range of tan δ_{max} is displaced towards high temperatures and is asymmetric. Analysis of the temperature variations recorded at a frequency of 1 Hz showed that, on heating and dissolution of film 2 in an organic solvent, the asymmetry increases and the range of tan δ_{max} values is divided into two peaks corresponding to tan δ_{max} for the initial copolymer and the copolymer enriched in MMA (curves *2'*, *2''*, and *2'''*), which indicates the presence in the latex particles obtained by seeded polymerisation of a transitional copolymer layer whose chemical composition is intermediate between those of the nucleus and the shell. It is formed at the beginning of the second stage as a result of the copolymerisation of the residual monomer of the seed latex with the monomers introduced in the second stage. On dissolution of the film in an organic solvent, this layer is removed from the interface between the segregated polymers and is segregated itself in a separate phase, which has been confirmed also by electron microscope data[106] (p.80).

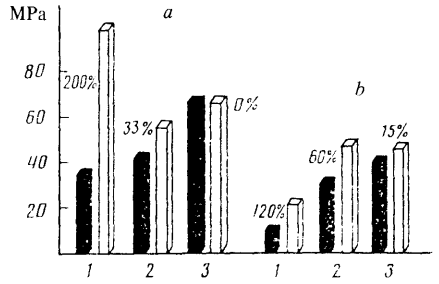


Figure 9. Breaking stress in the rupture of films made from latexes obtained by different methods before (filled columns) and after (open columns) prolonged storage[106] (p.124). Polymers: *a*) St–BA–MAA; *b*) MA–BA–MAA; the latexes were obtained by copolymerisation (*1*), by mixing the latexes (*2*), and by seeded polymerisation (*3*). The numerals in the diagram denote the increments in strength during the storage of the film.

The removal of the transitional layer from the interface between the segregated polymers lowers the mechanical strength of the films. Thus, after reprecipitation from an organic solvent of the film obtained by the seeded polymerisation of the latex having the general composition P(MMA–BA–MAA), its resistance to rupture is reduced almost by 30%[106] (p.94). The reprecipitation of a film having the same composition but obtained from a mixture of latexes does not alter its strength. Thus the presence at the interface of the composite particle of a transitional layer having an intermediate chemical composition increases the strength of the films: the presence of this layer improves the thermodynamic compatibility of the polymers in the core and the shell and intensifies the interchain interactions. The second cause of the increase in the strength of the films obtained from particles with the "core–shell" structure consists in the ordered distribution in them of a highly dispersed filler formed from the cores of the particles, which does not occur in the blended film. This improves the surface contact between the filler and the "shell"—the film matrix, on which interfacial interactions strengthening it take place.[107]

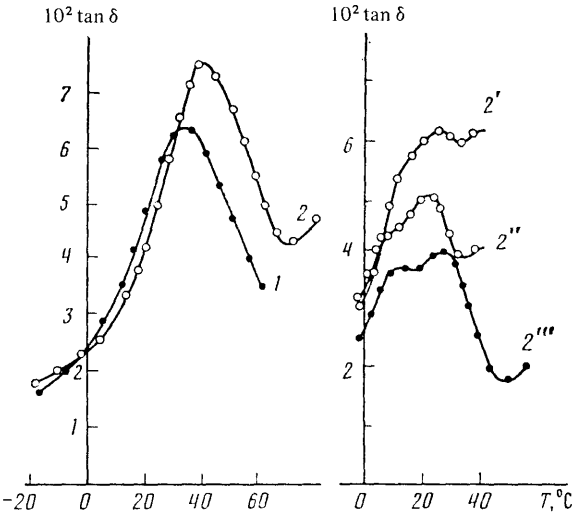


Figure 10. Temperature variation of tan δ at frequencies of 1 kHz (curves *1* and *2*) and 1 Hz (curves *2'*, *2''*, and *2'''*) for MMA–BA–MAA films formed in different ways: 1) from a mixture of the PMMA and P(MMA–BA–MAA) latexes; 2) and 2') from latexes obtained by the seeded polymerisation of the MAA–BA–MAA mixture on a PMMA latex; 2'') from the latex 2 after heating at 70 °C; 2''') from the latex 2 after reprecipitation from dioxan.[42]

The structures of the latex particles and films obtained by the joint and seeded polymerisation can be represented schematically, as shown in Fig.11. These schemes make it possible to understand the difference between the physical properties and behaviour of these materials after a long time has elapsed (Fig.9). The equilibrium structure of films produced from linear polymer latexes with homogeneous particles, obtained by the joint polymerisation of hydrophobi monomers, is produced in the course of the mutual diffusion of the molecules between the particles and the uncoiling of the macromolecules, which is accompanied by an increase in the strength of the films as a result of the increase in the number of intermolecular contacts[51] (Figs.9*a*–*1* and 9*b*–*1*). In films produced from latexes obtained by seeded polymeristion,[43,44] the mutual diffusion of the molecules is restricted in space mainly by the thickness of the layers of the elastic polymer between the nuclei of the filler. In the case of the vitreous state of the latter, equilibrium is attained already in the film formation process and subsequently the strength of the film does not vary with time (Fig.9*a*–*3*). In the case of an elastic filler, partly compatible with the matrix, limited mutual diffusion of the macromolecules takes place in the films as a function of time, which is accompanied by some increase in the strength of the film with time (Fig.9*b*–*3*).

The presence of a highly dispersed filler which is a foreign polymer limits the mutual diffusion process also in films made from blended latexes, but to a much smaller extent than in the case of films produced from latexes obtained by seeded

polymerisation, which can apparently be explained by the disordered distribution of the filler particles and the absence of transitional layers in the contact zone. The strength of the blended films increases with time (Figs. 9a–2 and 9b–2).

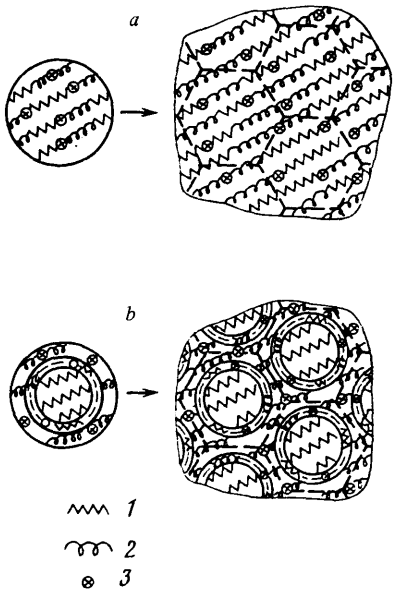


Figure 11. The phase structure of the particles and films formed from latexes obtained by the copolymerisation (a) and seeded polymerisation (b) methods: 1) PMMA; 2) PBA; 3) MAA.

The data presented in this Section on the phase structure of composite latex particles indicate a wide variety of factors influencing it and its relation with the properties of the polymers isolated from the latexes. The phase structure of the particles formed in seed polymerisation depends on the physical state and structure of the polymer of the seed latex, the parameters of its interaction with the monomers introduced in the following stage, the rate at which they are introduced, the degree of swelling of the seed particles in them, and the concentration of the emulsifier in the system, i.e. both on thermodynamic factors and on the specific features of the latex polymerisation process.[108] This process results in the formation of mixed structures, grafted copolymers, interpenetrating polymer networks, and segregated polymers in the form of concentric regions of the "core–shell" type.

In order to obtain graft polymers and systems of the INP type, the method of seed polymerisation with the simultaneous introduction of the monomers into the system is used preferentially. In the absence of an excess of emulsifier, this promotes the occurrence of polymerisation in the PMP formed initially[109] and the most complete chemical interaction (grafting) of the polymers.[48] The use of a semicontinuous seeded polymerisation method with gradual introduction of the monomers, in which equilibrium swelling of the seed particles in the latter is not attained, is a procedure for the specific formation of the particle phase structure of the "core–shell" type also when chemical bonds are not formed between the segregated polymers. The thickness of the shell and the degree of phase separation of the segregated polymers are regulated by choosing the ratio of the monomers in the first and second stages and the degree of conversion of the monomer in the seed latex.

In order to obtain a continuous film made up of composite particles consisting of polymers with different T_g, the bulk phase content of the more elastic component should be not less than 30–40%.[26] Such films are elastic polymer matrices filled with a highly dispersed filler consisting of a rigid polymer; they have a two-phase structure and thus differ significantly from the latex films incorporating homogeneous elastomer particles which ultimately form a single continuous phase.[49–52] The formation of a strong film from the latex always involves the formation of irreversible contacts at the initial interface between the particles, which is attained in the case of homogeneous particles as a result of the mutual diffusion of the macromolecules. The formation of a strong latex film consisting of heterogeneous particles requires in addition the attainment of an irreversible contact between the matrix and the filler. If there is no chemical binding, this takes place as a result of the formation of chemical or diffutional transitional layers between the segregated polymers. The strength of the two-phase films compared with the single-phase films of the same composition is greater owing to interfacial interaction; the MFT decreases simultaneously as a result of the localisation of the elastic component within the film matrix formed from the shells of the particles. Diffusional processes as well as reversible deformation, ensuring the elasticity of the system, are restricted in two-phase films by the thickness of the layers of the elastic matrix between the "cores" of the highly dispersed filler.

IV. LAYER FORMATION AND PHASE INVERSION IN COMPOSITE PARTICLES AND THE PROPERTIES OF THE "INVERTED" LATEXES AND FILMS

1. Effects Associated with the Separation of Phases into Layers

As stated above, one of the processes leading to the formation of composite particles is the polymerisation of the monomer 2 in the particles of the monomer 1 which had been swollen in it. In the final stage of the polymerisation, as the second polymer incompatible with the first is formed, phase separation takes place in the particles and is accompanied by a change in the shape of the particles and the segregation of a new highly dispersed fraction from them. When sufficiently strong transitional layers are formed between the components, the fragmentation of the particles is not observed.[48,110–113]

In composite particles having the same composition, the phase separation effects depend on the polymerisation method. Thus, in the seeded polymerisation of St on PMA, PEA, and PVA latexes, spherical particles are formed in most cases. However, after the preliminary equilibrium absorption of St in the seed latex, the particles acquire a "raspberry-like" shape and fragment at the end of the process: PSt domains appear initially in the seed particles and, after the attainment of 95% conversion, combine into cores which are subsequently segregated in the form of highly dispersed particles.[110] The latter explains the non-spherical shape of the particles and the intense local stresses arising in them as the latex is shaken in the polymerisation process.[110] When St was introduced gradually into the PBA or St–ethylene glycol dimethacrylate latex, the formation of "raspberry-like" particles was also observed but these did not break up on heating and shaking the latex. The transitional layers formed in this

process apparently ensure adequate adhesion of the segregated polymers. Conditions have been found (temperature, phase ratio) under which semispherical particles with cavities in their interior are formed as a result of the seeded polymerisation of St on PBA.[111,112] The observed effect is explained by phase separation: part of the polymer, enriched in PBA, "slips out" from the overall particle during the polymerisation process owing to inadequate adhesion.

The films obtained from latexes comprising particles of two incompatible polymers, with sharply different T_g, undergo a radical change in their physical properties as a result of heat treatment.[113] Thus, when films made from latexes obtained by the seeded polymerisation of St on the PEA latex were heated at a temperature above the T_g of the more rigid polymer (PSt), a change in their mechanical, adhesion, and optical characteristics was observed. The initial films were elastic, were characterised by a high adhesion capacity, and exhibited rainbow colours in both transmitted and reflected light; after heating, they became rigid, did not adhere to the support, and became cloudy. After reprecipitation from an organic solvent, there was no longer any change in the properties of the same films as a result of heat treatment. The thermal sensitivity of the films is controlled by altering the relative contents and the T_g of the constituent polymers. This effect can be explained by the morphological changes occurring in the latex film on heating, namely separation into layers and phase inversion: in the unheated film, the matrix is PEA, which ensures its elasticity and high adhesion capacity; after heating, the continuous phase becomes PSt, as a result of which the strength increases but the elasticity and adhesion capacity diminish. This phenomenon, which has also been observed by Kast,[114] is apparently associated with the free energy gained by the system as a result of the combination of the highly dispersed fraction of the polymer into larger domains and into one continuous phase.

2. The Influence of the Polarity of the Polymer on the Morphological Changes in Composite Particles

Stable latexes at a 30% concentration are formed in the emulsifier-free polymerisation of St on seeding the PEA latex subjected to preliminary hydrolysis in such a way that the surfaces of the seed particles contain carboxy-groups at a specified concentration with the ratio PEA : PSt = 2.5 : 47.5. Hydrolysis of the ester groups of PEA is achieved in the polymerisation of EA in an acid medium generated by the decomposition of the initiator—a persulphuric acid salt.[115]

Matsumoto and co-workers[71,115] investigated the mechanism of the formation of stable particles by electron microscopy at different stages of the polymerisation of St on the PEA latex taken in proportions of 1 : 1. At the beginning of the polymerisation, a fraction of fine PSt particles appears in the PEA seed particles, while at the end of the process particles of the type of "confetti" are produced (Fig.12). The authors explain this morphological picture by the diffusion of St radicals from the aqueous phase to the surface zone of the seed particles, where they grow by absorbing styrene: the macromolecules formed are combined into domains incorporated in the PA phase. Since particles in the form of "confetti" were not formed on replacement of St by the more polar MMA, it was concluded that the polarity of the polymer affects the phase structure of the composite particles. On the other hand, the stability of the polystyrene emulsifier-free latex, obtained by the polymerisation of St on the hydrolysed PEA latex, has been explained[71,115] by the distribution of the latter on the surface of the PSt particles and the orientation of the carboxy-groups at the interface with the aqueous phase.

The distribution of polymers in the bulk phase and on the surface of the particles as a function of the polymer polarity has been investigated in relation to the seeded polymerisation of compositions based on MA, MMA, and St.[35] The method involving the adsorption titration of the latexes with a solutin of sodium dodecyl phenylmethanesulphonate, the adsorption area of the molecules of which had been determined beforehand for homopolymer latexes, was used. It depends on the polymer polarity and amounts to 214, 133, and 53 Å^2 respectively. For statistical copolymers, this area is additive. The polymerisation conditions were chosen so that the number of particles did not change during the process. In the polymerisation of St on the PMMA seed latex, the ratio of these components in the surface zone of the particles did not correspond to their overall ratio in the system, as happens in copolymerisation: the concentration of PMMA on the surface of the particles was higher than in the system as a whole.

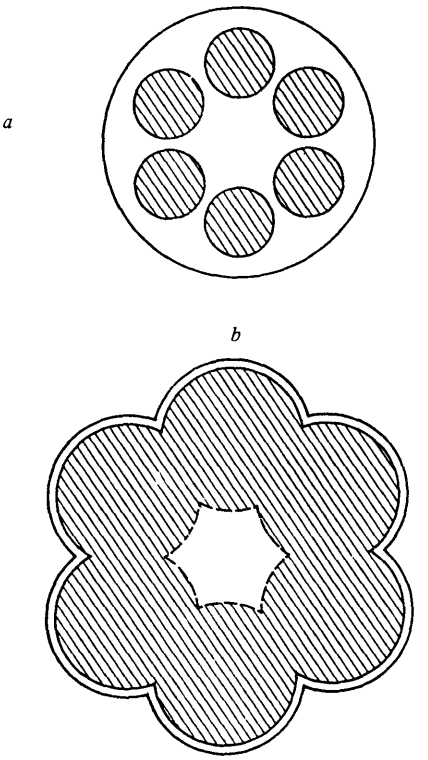


Figure 12. The shape of the particles formed in the seeded polymerisation of St on a PEA latex at the beginning (*a*) and end (*b*) of the process; open regions—PEA; shaded regions—PSt.[71,115]

The authors explain this behaviour[35] by the greater hydrophilicity of MMA compared with St. The hydrophilic properties were characterised by data on the interfacial tension of the polymer solutions in the same monomer at the interface with the aqueous phase. It proved to be 26.5 dyn cm^{-1} for the PSt/St solution and 12.6 dyn cm^{-1} for the PMMA/MMA solution. These data show that PMMA is adsorbed preferentially at the interface with the aqueous phase, compared

with PSt. An analogous but more clear-cut morphological picture was observed when the more polar PMA was used as the seed latex.

In a study of the seed copolymerisation of chloroprene (CP) and MAA (95:5) on the butyl methacrylate (BMA)–MAA (95:5) copolymer latex under the conditions of the gradual introduction of the monomers, the phenomenon of phase inversion in the colloidal particles was observed.[116] By following the mechanism of their formation with the aid of electron microscopy and contrasting the diene component with osmium tetroxide (Fig.13), it was shown that the PCP, formed in the second polymerisation stage in the form of domains (Fig.13*b*) or a separate phase (Fig.13*c*), is concentrated on the surfaces of the polyacrylate seed particles and is incorporated in their cores, the polymer of the seed latex then disintegrates and emerges onto the surfaces of the composite particles (Fig.13*d*) in the form of domains. Thus phase inversion takes place during polymerisation in the composite particles. This phenomenon has been explained by the free energy gained by the system on passing from the P(CP–MAA)–aqueous phase interface in the particles to the P(CP–MAA)–P(BMA–MAA) interface in the composite particles and the P(BMA–MAA)–water interface in the aqueous phase. The latter can be explained by the fact that the polarity (the contribution of the polar interactions to the interfacial tension) of PBMA is higher than that of PCP, the two polarities amounting to 0.18 and 0.11 respectively.[117]

Such phase inversions affect significantly the properties of latexes and films. This is indicated by the comparison of the properties of the latex described and the latex having the same composition but obtained by polymerisation in the opposite sequence. In the latter case, phase reversal does not occur and both latexes are characterised by similar morphologies of the particles.[118] The properties of latexes having the same composition but obtained with the monomers introduced in different order differ significantly: the "non-inverted" latex does not exhibit frost resistance, while the "inverted" latex withstands seven freezing (to −30 °C) and thawing cycles.[118]

The frost resistance of the inverted latex is apparently associated with the high concentration of carboxy-groups[119] and non-freezing water[120] on the surface of the particles. The concentration of carboxy-groups on the surface of the particles can be a result of their spontaneous energetically favourable orientation at the interface with the aqueous phase. Such orientation takes place during the disintegration of the P(BMA–MAA) copolymer of the seed latex and its emergence onto the surface in the form of domains. In the shells of the "non-inverted" latex particles, the carboxy-groups are distributed at random (in the second stage of the copolymerisation of BMA with MAA) and their concentration on the surface of the particles is lower. This hypothesis is confirmed by the significant increase in the strength and the sharp decrease in the absorption of water by the "inverted" latex film, which can be accounted for by the higher concentration of the interparticle hydrogen bonds formed between the carboxy-groups when the particles come into contact during film formation and hence by the denser structure of the film.

It has also been shown that, in the seeded polymerisation of Bd–St on the carboxylated EA–MAA (90:10) copolymer latex, phase inversion takes place in the second stage of the process in the particles, as a result of which the hydrophobic polymer comes to be located within the particles and the more hydrophilic polymer is in their peripheral zone.[121] The degree of emergence of the carboxylated polymer onto the surface of the particles has been investigated by the potentiometric titration method and it has been established that it depends on the molecular weight of the polymer. In the presence of $CHBr_3$ as the chain transfer agent, which is used to regulate the molecular weight in both stages, 92% of the MAA introduced was found on the surface of the particles, while in its absence the corresponding figure was only 69%. This is evidently associated with the greater mobility of the macromolecules with a lower molecular weight, which facilitates their emergence onto the surface of the particles.

The phenomenon of phase inversion in particles has been observed also in the seed polymerisation of acrylic monomers, which are characterised by different solubilities in water.[33] The MA–MAA (90:10) mixture was polymerised on the EA–MAA (90:10) copolymer seed latex and the EA–MAA (90:10) mixture was polymerised on the MA–MAA (90:10) copolymer seed latex. The ratio of the polymers was 1:1 in both cases. It has been shown with the aid of the NMR and

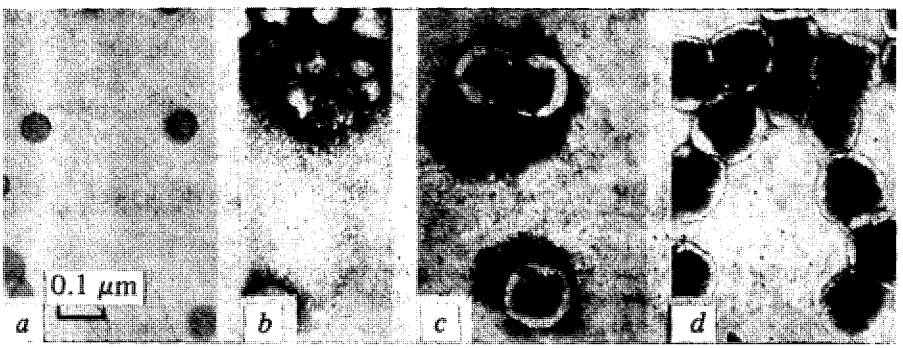


Figure 13. Electron photomicrographs of the particles formed in the CP – MAA seeded polymerisation on a P(PMA–MAA) latex; *a*) seed latex; *b*) and *c*) second stage of the polymerisation process; *d*) final latex.

acid titration methods that the peripheral zone of the particles of both latexes contains only PMA, while the core contains PEA and PMA, i.e. the more polar polymer is always present in the shell of the particles regardless of which monomers were polymerised in the first and second stages. Thus phase inversion occurred in the particles in the second case, as in the other systems described above.

Not only the polarity but also the physical state of the polymers is important for the phase transformations of this kind during latex polymerisation. Evidently the decrease in the Gibbs free energy, which promotes the "drawing" of the hydrophobic polymer into the interior of the particles, is possible only when the macromolecules of the seed and second polymers exhibit a sufficiently high translational mobility, i.e. when the polymerisation temperature T_{pol} is higher than the T_g of the polymers.

This conclusion has been confirmed in a study of the mechanism of the formation and phase structure of the particles of composite polymers obtained by the semicontinuous seeded polymerisation of CP on the PEA, PMMA, and PSt latexes.[122] The polarity of the polymers was estimated from the interfacial tensions of the monomers at the interface with water; in the cases indicated, they amounted to 16.9, 17.8, and 35.0 dyn cm^{-1} respectively. The physical state of the polymer in the polymerisation process was inferred from the differences $\Delta = T_g - T_{pol}$, which were 60, -65, and -60 K respectively. The selected polymers of the seeding latexes were either in the same vitreous state under the polymerisation conditions but differed in polarity (PSt, PMMA) or their polarities were similar but they existed in different physical states (PMMA, PEA). It was shown that, in the polymerisation of CP in the presence of all the seed latexes, PCP are formed initially (Fig.14), behaving differently in different cases. In the PCP–PSt composition, they aggregate into more stable particles, forming a separate fraction, apparently as a consequence of the sharp difference between the chemical natures of the polymers. In the PCP–PMMA composition, the PCP particles are adsorbed on the surface of the PMMA particles, forming a dense non-uniform shell: the rigidity of PMMA prevents the PCP domains from penetrating into the

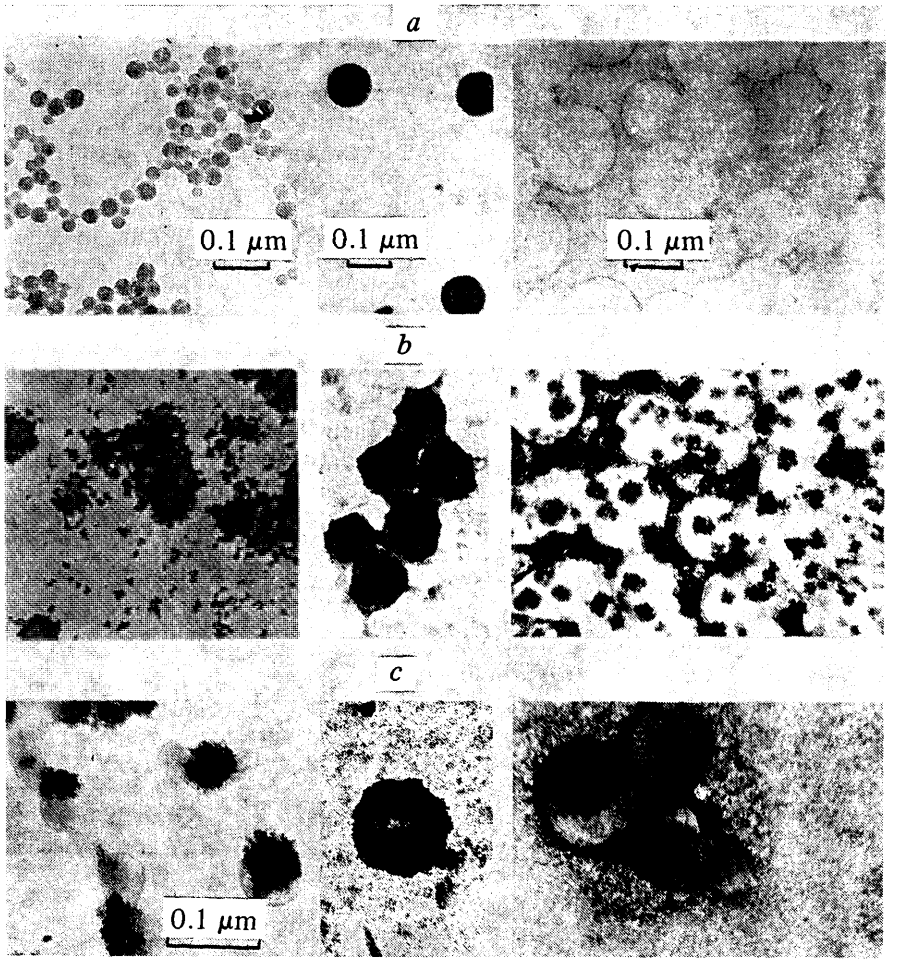


Figure 14. Electron photomicrographs of the particles formed in the seeded polymerisation of CP on PSt (*1*), PMMA (*2*), and PEA (*3*) latexes: *a*) seed latex; *b*) second stage; *c*) final latex.[122]

bulk of the particles, as happened in the case of PBMA (Fig.13). Finally, in the PCP–PEA composition, the PCP domains penetrated into the bulk of the seed particles, forming a discrete phase in the latter: in terms of polarity, PEA is close to PMMA, but during the polymerisation process it exists in a viscofluid state, as a result of which it does not prevent the "drawing" of the PCP domains into the bulk of the hydrophobic particles which is determined by thermodynamic factors.

The data presented in this Section show that the phase structure of the composite colloidal particles can undergo significant changes during polymerisation depending on the compatibility, polarity, and the physical state of their constituent polymers.

If the polymers are incompatible and a strong contact between them is not attained, phase separation takes place in the bulk of the particles: a discrete polymer phase appears, which can lead, under certain conditions, to a non-spherical shape of the particles, the segregation from them of a new highly dispersed fraction, and the formation of semispherical particles with cavities.

When the difference between the T_g of the incompatible polymers is large, the latexes with composite particles form thermosensitive films whose physical properties change sharply as a result of heat treatment. This is caused by the inversion of the polymer phases in the two-phase film, whose driving force arises from the endeavour of the system to reduce the area of the interface.

When the difference between the polarities of the polymers is large and the mobility of their macromolecules is adequate, phase displacement can occur in the polymerisation process of a kind such that, regardless of the sequence in which the monomers are introduced into the reaction system, the more polar component is on the surface of the particles. This phenomenon is associated with the gain of free energy on formation of a colloidal system with a smaller interfacial tension and entails an increase in the resistance of the latexes to aggregation.

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Summarising the data described in the review, one may reach the following conclusion. A characteristic feature distinguishing hydrophobic polymeric colloids—latexes and other hydrophobic sols—is the complexity and wide variety of the structures of the particles, which depends both on the chemical nature of the polymer and on many factors associated with the conditions governing their formation in the two-phase polymerisation system. The colloidal behaviour of the latexes and the kinetics of the latex polymerisation depend on the structure of the particles which have been formed and are being formed respectively. Being retained in the polymers and films isolated from the latexes, the structure of the particles has a decisive influence on their physical properties. In this sense, the most typical are the latexes of polymers modified by functional groups and the latexes of composite polymers. The presence of an interface with the aqueous phase, on which colloidal polymer particles are formed, is an important factor in both cases, which influences the orientation, packing, and distribution of the polymer molecules and domains, if the forces acting at this interface (dipolar interactions, hydrogen bonds) can compete with the intramolecular and intermolecular interactions of the macromolecules, i.e. if the macromolecules in the PMP are sufficiently mobile.

The physicochemical film formation process, which has been investigated for the latexes of elastomers with homogeneous particles,[49,52] in the case of latexes with heterogeneous particles must be considered taking into account the structure of the latter, where not single-phase but two-phase polymer systems with characteristic properties are formed as a result of the combination of the particles.

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Topological Indices in Organic Chemistry

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The numerical characteristics of molecular structures, called topological indices, which are used for the quantitative description of the structures of organic compounds, are examined. The method of topological indices is analysed as one of the procedures for determining the relation between the structure of chemical compounds and their properties.
The bibliography includes 164 references.

CONTENTS

I.	Introduction	191
II.	Topological indices as quantitative characteristics of molecular structures	193
III.	The use of topological indices for the estimation of physicochemical properties of compounds	199
IV.	Topological indices and biological activity	201
V.	Quantum-chemical methods as a source of topological indices	202

I. INTRODUCTION

The search for regularities in the type of variation of different properties of molecules as a function of their structure belongs to the so called "structure–property" problem which has long attracted the attention of chemists.[1-2] The solution of this problem even for an individual fairly narrow range of compounds is extremely important.[3] The observed regularities can be used for the systematic treatment of molecules of a given class, for the prediction of the properties of hypothetical molecules, and for the search for new compounds with a specified set of properties. Furthermore, they can also prove useful in the development of a theory which would explain the phenomenon under consideration and would provide a key to the understanding of the mechanism of the action of biological active compounds.

In order to find quantitative relations between structure and property, various mathematical modelling methods are used, their choice being determined by the type of chemical compounds, their state of aggregation, and the property being analysed. Procedures for the description of molecular structures occupy a special place among these methods.

The description of molecular structure can be detailed to different extents. Thus the overall formula shows how many and what atoms are contained in the molecule. The structural formula contains information also about the way in which these atoms are linked to one another. Finally, the specification of the coordinates of the atomic nuclei in space makes it possible to construct three-dimensional models of molecules. With the aid of quantum-chemical calculations, it is possible to obtain additional information about the distribution of electron density in the molecule. The physicochemical parameters reflecting the molecular structure indirectly are used in many cases to characterise the molecules.

Modern experimental research methods make it possible to determine fairly reliably the geometry and different physicochemical characteristics of molecules. However, such methods are applicable only to substances which actually exist and not to all substances. In those cases

where experiment is difficult, one can use quantum-chemical calculations of the geometrical and energy characteristics of molecules. Such calculations are still inferior as regards accuracy to experimental data and, moreover, they are associated with considerable computational difficulties. More formal and simpler methods, based on the description of the molecular structure by the structural formula, are therefore also used nowadays to solve the "structure–property" problem. In this topological method for the description of molecular structure, account is taken only of the types of atoms and of the character of their bonding to one another, but the metric characteristics of the molecule are neglected.

The methods based on the analysis of the structural formula in order to discover the relation between the structure and property have long been used in theoretical organic chemistry. For example, the additive schemes employed to estimate the physicochemical properties of hydrocarbons, based on the concept of a numerical characteristic of the property investigated in the form of the sum of the contributions by atoms and bonds, are widely known.[4,5] Further development of the topological approach led to the appearance of various modifications of simple additive schemes associated with allowance for a non-valence interaction, the use of more complex structural fragments, the application of non-linear functional relations between the property and the structural parameters,[6–10] etc. This made it possible to extend significantly the list of properties investigated and also to analyse compounds with a structure more complex than that of hydrocarbons.

The development of the topological approach is associated to a large extent with the application of the methods of graph theory,[11] since the structural formula of a molecule is equivalent to the corresponding molecular graph. The analysis of the structural formula which must be carried out within the framework of the "structure–property" problem therefore reduces to the treatment by the methods of the theory of graphs of the corresponding abstract mathematical structure—the molecular graph (MG). Weighted MG are usually employed in structural chemistry.[10] The weighting factors for the vertices and edges are chosen in order to take into account the differences between the types of atoms and bonds. The weighted graph is defined by the adjoining matrix $A = (a_{ij})$, $(i,j = 1,\ldots,n)$, where a_{ii} is the weighting factor of the ith vertex, $a_{ij} = a_{ji}$ the weighting factor of the edge (i,j), $a_{ij} = a_{ji} = 0$ if the vertices i and j are not connected by an edge, and n is the number of vertices in the graph. The form of the adjacency matrix depends, generally speaking, on the way in which the vertices of the graph are numbered. However, different numbers characterising its structure and independent of the way in which the vertices are numbered can be attributed to each graph. Such numbers are called the invariants of the graph or structural constants. Examples of the graph invariants are the number of vertices, the number of edges, the number of paths of equal length, the determinant of the adjacency matrix, etc. In organic chemistry, the invariants of weighted molecular graphs are called topological indices (TI). Topological indices have found a wide variety of applications in structural chemistry. In particular, they can be used to code chemical information, in designing a chemical experiment, in the theory of the atomic structure and reactivity of molecules, and for the quantitative description of chemical structures in the analysis of the relation between the structure of a molecule and its properties. In the present review, we shall discuss the last two applications of the TI.

As a rule, in order to establish a relation between the structural parameters $x_i, \ldots, x_k$ (in the given case topological indices) and the numerical characteristics of a property "y", a functional relation of the type $y = a_0 + \sum_i a_i x_i$, where a_i are unknown constants determined by the method of least squares, is sought. The quality of the model constructed is characterised by the regression parameter s (the standard deviation of the regression line; $s \geq 0$) and r (the correlation coefficient; $0 \leq r \leq 1$). In more general cases, non-linear functional relations are used.[12]

Another approach to the "structure–property" problem associated with TI is also possible. Its essential feature consists in the fact that the concept of "distance" between the structures is introduced on the basis of the TI, making it possible to estimate the similarity of the structures and to relate it to changes in the property considered. Furthermore, TI are used as structural descriptors in the solution of the "structure–property" problem by other methods, for example, by the image recognition method.[12]

The approach to the solution of the "structure–property" problem based on TI has a number of advantages, which include, firstly, the simplicity and rapidity of the calculation of TI even on small computers and, secondly, the non-empirical character of the indices and the possibility of obtaining them directly from the structural formula. The latter is especially significant when one is dealing with the estimation of the properties of hypothetical structures for which there are no experimental data whatsoever.

The method of topological indices, based on the formal description of the molecular structure, suffers also from an evident disadvantage: not all the characteristic features of the molecular structure are taken into account. Nevertheless, in many cases TI are satisfactorily correlated with both steric parameters (molecular volume, molecular refraction, the surface area of the molecule) and the electronic parameters (ionisation potentials, electron affinity, polarisability, chemical shifts in NMR spectra, spin density, etc.). Furthermore, in constructing TI one can take into account not only the topology of the molecule but also certain features of its electronic and steric structures, the weighting factors for vertices and edges of the MG being appropriately selected.

One should also note that TI are usually obtained with the aid of formal operations on the MG. It is therefore not always possible to achieve a satisfactory physical interpretation of certain TI and to explain the correlation obtained with their aid even at a qualitative level. In the solution of the specific problems with the aid of the TI method, the problem of the motivated [subjective?] selection of topological indices arises.

However, in certain applied fields, in particular in the search for new biologically active substances,[12,13] a fairly complex situation arises, associated with the necessity to synthesise and investigate a large number of chemical compounds. Therefore any even indirect considerations which enable the investigator to solve *a priori* the question of the structures which can have the required properties or those which need not be considered at all is of great interest. The TI method can be used in the solution of problems of this type as a "coarse filter" for the preliminary sorting of molecules.

Recently there has been considerable growth of interest in topological indices. Numerous publications on this topic have been published in which increasing numbers of new TI have been introduced (see, for example, Bonchev[14]). Naturally, the abundance of TI combined with the lack of a single theory makes it difficult to understand them, promotes the appearance of speculative publications in this field, and even to some extent discredits the TI method.

The main aim of the review is to carry out an approximate classification of the TI described in the chemical literature, to give an account of the general principles of the construction of TI, and to analyse the real possibilities of the TI

method as a procedure for the description of chemical structures in the solution of the problem of the "structure–property" relation. The review also discusses the relation between different indices and their interpretation. The individual Sections are devoted to the discussion of correlations of TI with physicochemical properties and with the biological activity of certain classes of compounds known from the literature.

There exists a series of foreign reviews devoted to the use of TI in structural chemistry.[14–19] However, these publications cover inadequately the different applications of TI and provide as a rule merely a description of the factual data without its analysis.

II. TOPOLOGICAL INDICES AS QUANTITATIVE CHARACTERISTICS OF MOLECULAR STRUCTURES

This Section gives a brief description of the principal ways of constructing TI used in the analysis of molecular structure.

1. Invariant Sets of Molecular Graphs

We shall denote by G an arbitrary molecular graph. Different sets of numbers (numerical sets) can correspond to the graph G, characterising its structure and being independent of the numbering of the vertices. Each such set $\mathfrak{M}$ will be called an invariant set (IS) of the graph G assuming, to make the treatment concrete, that its elements are arranged in a decreasing sequence. For example, the set of the elements of the adjoining matrix $A=(a_{ij})$ of the graph G as well as the set of degrees of vertices v_i, where

$$v_i=\sum_{j,j\neq i} a_{ij}.$$

are invariant sets. When the weighting factors of the edges are equal to the multiplicities of the corresponding bonds, the quantity v_i is equal to the number of edges incident with the vertex i and related directly to the valence of the ith atom.

Together with the adjacency matrix, other matrices corresponding to the graph G can be used to construct its IS. The distance matrix $D = (d_{ij})$ $(i,j = 1, \ldots, n)$, whose element d_{ij} is equal to the distance between the ith and jth vertices, is most often used in structural chemistry. The quantity d_{ij} is defined as the minimum number of edges which must be traversed when moving along the edges of the graph from the ith vertex to the jth. The set of elements of the matrix D, the set of the distance degrees of the vertices d_i, where

$$d_i=\sum_j d_{ij},$$

and also the spectra of the matrices A and D are IS. Other examples of IS will be examined below.

A whole family of different TI corresponds to each IS $\mathfrak{M}$. We shall describe several ways of constructing TI of this type.

First method. Suppose that the IS $\mathfrak{M}$ of the graph G consists of k elements $m_1, \ldots, m_k$. We shall select an arbitrary symmetrical function $F(x_1,\ldots,x_k)$ of k variables (the values of this function do not change in arbitrary transpositions of the arguments). The quantity $F(m_1,\ldots,m_k)$, regarded as the value of the function F on the graph G, is a TI corresponding to $\mathfrak{M}$. For example, if $\mathfrak{M}$ consists of the element of the adjacency matrix A of the graph G, $k = n^2$ (where n is the number of vertices of the graph G), and

$$F(x_1,\ldots,x_k)=\sum_i x_i,$$

then $F(m_1,\ldots,m_k)$ is equal to the sum of all the elements of the matrix A. If the graph G is simple, i.e. A is a matrix consisting of zeros and ones [a(0,1)-matrix] and $a_{ii}=0$, then $F(m_1,\ldots,m_k) = 2q$, where q is the number of edges of the graph. By altering the form of the function F, it is possible to construct a whole series of other TI also related to the given IS $\mathfrak{M}$. . In yet another example, we may specify a TI generated by the function

$$F_a=\sum_i \delta(x_i),$$

where $\delta(x_i) = 1$ for $x_i = a$ and $\delta(x_i) = 0$ for $x_i \neq a$, a being a fixed number. The value of the function F_a at the point $(m_1,\ldots,m_k)$ is equal to the number of elements of the set $\mathfrak{M}$ identical with a. Thus, if $a = 2$ and the IS consists of the elements of the matrix D, then the value of the function F_a is equal to twice the number of pairs of the vertices of the graph located at a distance of 2.

Second method. We differentiate in the graph G the subgraphs G_j of a specific type with the same numbers of vertices m $(m < n)$. We relate to the subgraph G_j the IS $\mathfrak{M}_j$ consisting of k elements: $m_1^{(j)},\ldots,m_k^{(j)}$. We select a symmetrical function $F(x_1,\ldots,x_k)$ of k variables. For each subgraph G_j, we find the value of $F(m_1^{(j)},\ldots,m_k^{(j)})$ and then we determine the TI equal to the sum of these quantities. In particular, if $F(x_1,\ldots,x_k) \equiv 1$, then the TI determined by the method described is equal to the number of subgraphs of the given type.

Third method. New TI can be obtained from those already known by adding, multiplying, subtracting, and dividing the latter. Finally, it is possible to construct a multi-index—an ordered sequence of simple indices.

The TI described above characterise the graph as a whole. Such TI are represented in many cases as the sums of the numerical characteristics of different structural fragments, for example, the vertices or edges of the MG and these characteristics are independent of the numbering of the vertices of the fragment. Some of these invariants, called TI of the local type, are of independent interest and are used in the solution of various problems in theoretical chemistry. For example, the local TI determined as the matrix elements of different functions of the adjacency matrix are used in the theory of the electronic structure of conjugated molecules.

2. Indices Related to the Distance Matrix D

Correct estimates of the dimensions and degree of branching of the molecule are important in the estimation of a number of physicochemical properties of compounds, for example, the boiling point or melting point, because the energy of intermolecular interactions actually depends to a considerable degree on these parameters. In the topological approximation, mainly indices characterising the "size and form" of the graph are used for the solution of this problem. Some of them are directly related to the distance matrix D. This approach was first applied by Wiener,[20] who suggested that two TI, W and p, defined in terms of the distances between the vertices of the corresponding molecular graphs, be used for the comparison of the carbon skeletons of saturated hydrocarbons. The index p is equal to the number of pairs of vertices the distance between which is 3 and W is equal to the sum of the distances between all pairs of vertices of the graph G. The number W, usually called the Wiener index, is expressed in terms of the elements of the distance matrix D by the formula

$$W=\frac{1}{2}\sum_{i,j}d_{ij}.$$

The index W can also be written in the form

$$W=\sum_{j}jg_j,$$

where g_j is the number of pairs of indices separated from one another by the distance j, i.e. the number of elements d_{kl}, $(k<l)$ in the matrix D equal to j.[21] The number p is identical in the given instance with the quantity g_3. The polynomial

$$W(x)=\sum_{j}x^jg_j,$$

introduced by Altenburg,[22] is sometimes used to characterise the distances between the vertices of the MG which can occur in the graph. In terms of the $W(x)$ polynomial, the Wiener index is calculated by the formula

$$W=\frac{dW(x)}{dx}\Big|_{x=1}.$$

The distance matrix is also used to determine the distance polynomial

$$D(x)=(-1)^n\det(D-xE),$$

where E is a unit matrix.[23] This polynomial is the invariant polynomial of the graph.

The indices $J(G)$ and $D^{(k)}$, associated with the matrix D, are described by the formulae†[13]

$$J(G)=\frac{q}{1+c}\sum'(d_id_j)^{-1/2}$$

$$D^{(k)}=\left[\left(\sum_i g_i\cdot i^k\right)\Big/\left(\sum_i g_i\right)\right]^{1/k};\ k=1,2,3,4,$$

where q is the number of edges and c is the cyclomatic number which in the case of simple graphs is equal to $q-n+1$.

In constructing certain TI, the concept of the centre of the graph is used.[11] The centre of the graph is defined as follows. For each vertex of the graph, one calculates initially the quantity $e_i=\max_j d_{ij}$, where i is the number of the vertex. The quantity e_i is called the eccentricity of the ith vertex. Then, among all the numbers e_i, the smallest is selected: $r(G)=\min_i e_i$. This number is called the radius of the graph. By definition, the centre of the graph is understood as the set of vertices whose eccentricity is $r(G)$. For example, the tree has a centre consisting of one or two connected vertices.[11] The centric TI for the tree is determined by means of the following procedure. In the first step, all the first degree vertices (pendant vertices) and the edges incident with them are cut off from the tree. In the second step, all the first degree vertices and the edges incident with them are again cut off from the subgraph obtained in the first step. This procedure is continued until finally only the central vertices of the tree remain. We shall denote by Δ_i the number of vertices eliminated in the ith step and shall put

$$B=\sum_i\Delta_i^2.$$

The quantity B is called the centric Balaban index.[24] The normalised (B') and binormalised (B'') centric indices are also defined in terms of the index D:

$$B'=0.5(B-2n+u),\ B''=2B'((n-2)^2-2+u)^{-1},$$

where $u=0.5\,[1-(-1)^n]$. A definition of the TI B_c, also related to the concept of the centre of the graph, has been proposed.[25] The index B_c is defined in terms of the formula

$$B_c=\sum_i r_i^2,$$

where r_i is the distance from the ith vertex to the centre. The centric indices B and B_c can also be defined in a different way in terms of the IS of the graph. Suppose that the set $N=(i_1,\ldots,i_k)$ consists of the numbers of central vertices. For each vertex i, one finds its distance from the centre $r_i=\min d_{ij}$ (j N; $r_i=0$ for the central vertices). The set of such numbers r_i constitutes the IS. Next the symmetrical function

$$F=\sum_{i=1}^{n}x_i^2,$$

defined by this IS, is calculated. As a result, one obtains the topological index B_c. The calculation of the index B reduces the calculation, for this IS, of the number of elements equal to $a=0,1,2,\ldots$.

The invariants of the graph, associated with the distances matrix D, have also been discussed in two other studies.[26,27]

We may note that the TI defined above refer to a simple molecular graph. In order to take into account heteroatoms and multiple bonds, the distance matrix D, constructed taking into account the weighting factors attributed to the vertices and edges of the MG, was introduced.[28] The elements of the matrix D were determined from the formulae

$$d_{ii}=1-\frac{6}{z_i}\ \text{and}\ d_{ij}=\sum\frac{1}{b_{kl}}\frac{36}{z_k\cdot z_l},$$

where z_j is the nuclear charge of the jth atom and b_{kl} the multiplicity of the bond (k,l); $b_{kl}=1$, 2, 3 or 3/2 depending on whether the bond is respectively single, double, triple, or aromatic. The summation is extended over all the bonds (k,l) forming the shortest path between the ith and jth vertices. The question of certain modifications of the distance matrix D in the presence of multiple bonds is also discussed in the above study.[29] In particular, it is suggested that a weighting factor equal to the bond length be attributed to each edge of the corresponding molecular graph.

3. Indices Based on the Invariant Set of Degrees of Vertices

Here we shall discuss certain TI which are defined in terms of the degrees of the MG vertices. Indices of this type can be easily calculated both for simple and weighted graphs. For this reason, they belong to the class of the most popular TI in theoretical chemistry. We shall indicate initially a series of indices (M_1,[30] P,[31] I,[14] and Q[24]) which are defined with the aid of symmetrical functions of degrees of the graph vertices of the type

$$\sum_i x_i^2,\ \prod_i x_i,\ \sum_i x_i$$

$$M_1=\sum_{i=1}^{n}v_i^2,\ P=\prod_{i=1}^{n}v_i,\ I=\sum_{i=1}^{n}v_i=2q,$$

$$Q=0.5\sum_{i=1}^{n}(v_i^2-2v_i)+1=0.5M_1-2q+1.$$

†In the formula for $J(G)$ and henceforth, the prime before the summation symbol implies that the summation is carried out with respect to all the edges (i,j).

We shall now assume that the edges have been selected as the subgraphs of the graph G in order to determine the indices. Using various symmetrical functions of two variables $F(x_1, x_2)$, it is possible to determine a series of TI which depend on the degrees of the vertices of the graph G. For example, the indices f, M_2, and χ have been introduced:[30,32,33]

$$f = {}'\sum(v_i + v_j - 2),$$

$$M_2 = {}'\sum v_i v_j,$$

$$\chi = {}'\sum(v_i v_j)^{-1/2}.$$

The quantity χ is called the molecular connectivity index or the Randić index,[33] M_2 is the Gutman index,[30] and f is the Platt index.[32] An extension of the structural parameter χ has been proposed;[34] the resulting index is called the index of molecular connectivity of order h. This graph invariant ${}^h\chi$ is determined from the formula

$${}^h\chi = \sum(v_{i_1}, v_{i_2}, \ldots, v_{i_{h+1}})^{-1/2} \text{ (along paths of length } h),$$

where $h \geq 1$ is a fixed integer and v_{i_k} is the degree of the vertex i_k along the given path of length h ($k = 1, \ldots, h$). Evidently, ${}^1\chi = \chi$.

The index ${}^h\chi$ was further modified[35,36] by differentiating in the graph G tree-like subgraphs G_j of a special type, each containing h edges. A certain number δ_i (for example, $\delta_i = v_i$) is ascribed to each vertex i of the graph G. Then the quantity

$$F(\delta_{j_1}, \ldots, \delta_{j_{h+1}}) = \prod_{k=1}^{h+1} \delta_{j_k}^{-1/2},$$

is calculated for each subgraph G_j with the vertices $j_1, \ldots, j_{h+1}$. The numbers $F(\delta_{j_1}, \ldots, \delta_{j_{h+1}})$ are then summed over all the subgraphs G_j. In order to take into account multiple bonds and heteroatoms, it has been suggested[36,37] that the quantities

$$\delta_i = z_i^v - r_i \quad \text{or} \quad \delta_i = (z_i^v - r_i)/(z_i - z_i^v - 1),$$

where z_i and z_i^v are respectively the total number of electrons and the number of valence electrons in the ith atom and r_i is the number of hydrogen atoms linked to the ith atom, be used as the numbers δ_i. The connectivity indices obtained in this way may be called the valence connectivity indices and are denoted by ${}^h\chi^v$.

However, cases are possible where atoms of one kind, forming bonds of different types with their neighbours, cannot be distinguished with the aid of the number δ_i. For this reason, a "perturbation" connectivity index has been introduced.[9] Instead of δ_i, in each construction use was made of the numbers δ_i^p, which are determined from the equation $\Gamma\overline{\delta^p} = \overline{\delta}$, where $\overline{\delta^p}$ and $\overline{\delta}$ are column vectors with the components δ_i^p and δ_i ($i = 1, \ldots, n$), respectively and $\Gamma = (\gamma_{kl})$, where $kl = 1, \ldots, n$, is a square matrix. The matrix elements γ_{kl} satisfy the conditions $\gamma_{kk} = 1$ and $\gamma_{kl} = 0$, provided that the vertices k and l are not connected. In the remaining cases, the γ_{kl} are selected empirically. Examples of correlations of different physicochemical properties with the "perturbation" connectivity index for a special selection of the elements of the matrix Γ (for example, for $\gamma_{kl} = \gamma_{lk} = 0,1$) have been published[9] and it has been noted that the quality of the correlations is higher than in the case where "non-perturbation" quantities δ_i are used.

The index χ has also been modified in a study[38] whose authors introduced the concept of the lth order connectivity K_l, where $l = 2,3$, using the following formula to find this quantity:

$$K_l = {}'\sum((v_i a_i v_j a_j) b_{ij})^{-1/2},$$

where ${}^l v_i$ is the number of second-order ($l = 2$) or third-order ($l = 3$) neighbours of the vertex i, the number a_i characterises the type of the ith atom, and b_{ij} is the (i,j) bond order. The indices ${}^1\chi$, ${}^2\chi$, f, and M_1, determined for weighted graphs, have been discussed.[29]

In the case of weighted graphs, the problem of the choice of the weighting factors for the vertices and edges arises. Some of the ways of introducing the weighting factors were discussed above. One of the possible variants of the distribution of the weighting factors among the vertices of the graph, associated with the method of potentials,[40] has been proposed.[39] A number u_i, called the potential defined by the formula

$$u_i = \sum_{j=1}^{n} h_{ij} h_{jj},$$

where $i = 1, \ldots, n$ and the h_{ij} are the elements of a non-degenerate matrix $H = (h_{ij})$, which depend in a special way on the elements of the adjoint matrix, is attributed to each vertex. The topological index is defined by the expression

$$\prod_{i=1}^{n} u_i \text{ [39].}$$

Certain TI which depend on the degrees of the vertices, can be represented as functions of the TI associated with more complex fragments. For example, $f = 2N_2$, where f is the Platt index and N_2 the number of paths on the MG whose length is 2 (the quantity N_2 has been introduced as the TI in the study of Gordon and Scantlebury[41]). On the other hand, if the degrees of the graph vertices do not exceed 4, then the index N_2 is linearly related to the index Q and the index M_1: $Q = N_2 - n + 2 = 3 - 2n + 0.5M_1$. For acyclic graphs,

$$\sum(v_i - 1)v_i \text{ [16].}$$

The index N_2 has been used to construct a new topological index ${}^2\kappa$ on the basis of the formula

$${}^2\kappa = \frac{2N_{2,\max} \; N_{2,\min}}{N_2^2},$$

where $N_{2,\max} = 0.5(n-1)(n-2)$ and $N_{2,\min} = n - 2$ are the values of N_2 for a simple chain and a star respectively and n is the number of vertices of the graph.[42]

The MG fragments corresponding to paths whose lengths are greater than 2 have also found applications in the construction of TI.[8,43-45] For example, it has been suggested that the sequence of numbers $N_1, \ldots, N_k$, where N_i is the number of paths of lengths i on the MG, be used to code chemical structures.[43-45] The "distance" d between the structures can be determined in terms of the numbers N_i by means of one of the formulae

$$d^2 = \sum_i (N_i - N_i')^2 \text{ and } d = \sum_i (N_i - N_i') \log_2 \frac{N_i}{N_i'},$$

which makes it possible to classify these structures in terms of the extent to which they approach a certain standard structure. In many cases the sequence of structures obtained in this way is consistent with the character of the changes in the properties.[43,45]

4. Indices which Depend on the Spectroscopic Characteristics of the Graph

A series of TI used in the analysis of molecular structures are related directly to the eingenvalues λ_j, where $j = 1, \ldots, n$, of the adjacency matrix A of the molecular graph.

The numbers $\lambda_1, \ldots, \lambda_n$ form the spectrum of this graph and are identical with the set of zeros of the characteristic polynomial:[23]

$$R(G, x) = (-1)^n \det(A - xE) = x^n + a_1 x^{n-1} + \ldots + a_n .$$

The spectrum of the graph is an IS and the coefficients of the polynomial $R(G,x)$ are symmetrical functions of the eigenvalues. Therefore any coefficient of the polynomial $R(G,x)$ can be used as the TI. In particular, the sum of the absolute coefficients of the polynomial

$$\sum_i |a_i| .$$

is also a TI. For acyclic graphs, this quantity is identical with the Hosoya index Z:[46]

$$Z = \sum_k p(G,k) ,$$

where $p(G,k)$ is the number of ways of selecting k edges of the graph in such a way that no two of them have common vertices. The Hosoya indices used for the estimation of the physicochemical properties of hydrocarbons have been tabulated.[47,48]

Individual eigenvalues, the sums of non-negative eigenvalues, etc. are also used as the TI.[44,49,50] For example, the maximum eigenvalue is used as the characteristic of the degree of branching of the molecule.[49] The relation between the coefficient of the polynomial $R(G,x)$ and other invariants of the MG has been discussed.[23] The spectroscopic characteristics of MG have found applications in the theory of the electronic structures of conjugated systems. These questions are considered in greater detail in Section IV.

5. Information Topological Indices

One of the ways of comparing molecular structures in terms of the topological approximation consists in the calculation for each of them the number of structural fragments of a specific type and subsequent comparison of these quantities. Since the structural fragments of one type can differ in terms of some feature, they can be classified further with different degrees of detail. We shall assume that a certain criterion has been selected for the classification, which leads to the subdivision of the set of the chosen structural fragments X, consisting of n elements, into k equivalence classes X_i, and

$$n = \sum_i n_i ,$$

where n_i is the number of elements in the set X_i. Definite information about the molecular structure, which can be characterised quantitatively, is associated with each selection of the numbers $(n_i, \ldots, n_k)$. The quantity n_i/n can be regarded as the probability of finding the fragment from the class X_i in the structural formula of the molecule considered. Therefore, for a quantitative assessment of the information about the molecular structure contained in the set of numbers $(n_1/n, \ldots, n_k/n)$, use is made of the entropy of the distribution of the probabilities $\bar{I}$ and the associated quantity $I = n\bar{I}$, which are calculated from the formulae

$$\bar{I} = -\sum_i \frac{n_i}{n} \log_2 \frac{n_i}{n} , \quad I = \bar{I}n = n \log_2 n - \sum_i n_i \log_2 n_i .$$

The quantities $\bar{I} \geq 0$ and $I \geq 0$ can be used to estimate the degree of inhomogeneity of the set of the selected structural fragments of the molecule. This method of interpretation is based on the following properties of the entropy: for the most inhomogeneous subdivision (i.e. when $n_i = 1/n$, $i = 1, \ldots, n$), the quantity $\bar{I}$ assumes its maximum value, which is $\log_2 n$, while for the most homogeneous subdivision (i.e. when one of the numbers n_i is 1 and all the others become zero), $\bar{I}$ attains its minimum value, which is zero. The function $\bar{I}$ is sometimes referred to as the average information content of the given subdivision and I is the information content of the subdivision. The use of such terminology is associated with the fact that in information theory formulae of a similar type are used to characterise the amount of information contained in a message of a special type. The specification of the number n_i/n can be interpreted as a message about the composition of the set X. Furthermore, the formula for the index $\bar{I}$ is analogous to the expression for the thermodynamic entropy.[51]

At the present time, a series of TI, referred to as the information TI, are used in structural chemistry. All these indices are constructed in accordance with the principle described above: initially a certain set X, consisting of the structural fragments of the molecular graph, is selected and then it is subdivided into equivalent classes X_i and the quantities I and $\bar{I}$, which depend on the chosen set of structural fragments and the criterion constituting the basis of the subdivision of the set X into classes, are calculated. We may note that the methods used to construct quantities of the type I and $\bar{I}$ fit within the general scheme for the construction of TI described in subsection 1. In this case, the set $= (n_1/n, \ldots, n_k/n)$ is an IS and the symmetrical function F has the form

$$F(x_1, \ldots, x_k) = -\sum_i x_i \log_2 x_i .$$

We shall deal brirefly with certain TI of the information type used in the analysis of molecular structures.

(a) Allowance for the atomic composition in the wide variety of types of chemical bonds. The information indices were first used in theoretical chemistry in a study[52] where the assembly of all the atoms of the molecule was considered as a set X and the assembly of atoms of a single type i were treated as the subsets X_i. The degree of inhomogeneity of the elemental composition was characterised by the information-theoretic index I_{at}. Subsequently the index I_{at} was modified;[53] apart from the elemental composition, account was taken also of the valence of the atoms. The inhomogeneity of the molecular structure was then estimated with the aid of the Morowitz formula

$$I_{MOR} = I_{at} + \sum_i n_i \log_2 t_i ,$$

where the numbers t_i are calculated from the valences of atoms of the ith kind. The index I_B, characterising the variety of chemical bonds, was determined analogously:[54]

$$I_B = B \log_2 B - \sum_i B_i \log_2 B_i ,$$

where B_i is the number of bonds of type i (for example, single, double, and triple) and B is the total number of bonds.

(b) Allowance for the symmetry of the molecular graph. It has been suggested[55-57] that the vertices of the graph be subdivided into equivalence classes in such a way that the vertices of different classes cannot be interconverted whatever the automorphism of the graph. For example, it is possible to combine in a single class vertices having the same degrees, the same number of second neighbours, etc. The "finest" subdivision is generated by the orbits of the group of automorphisms of the graph. The information index I_{orb} corresponds to such subdivision into classes. In order to characterise the molecular structure, the sum of the automatic and orbital indices has been introduced:[55]

$$\bar{I}_{RASH} = \bar{I}_{at} + \bar{I}_{orb}.$$

(c) Chromatic information index. The graph G is said to be k-colourable if its vertices can be coloured by k colours in such a way that each vertex has neighbours of another colour only.[11] The vertices of a graph coloured in this way can be divided into non-intersecting classes. The elements of each class have the same colour and are not connected. The smallest number $k = k(G)$ for which k-colouring of the graph is possible is called the chromatic number and the corresponding subdivision into classes is called the chromatic resolution of the vertices.

Suppose that V is the chromatic resolution of the vertices of the graph and $n_i(V)$ the number of vertices in the ith class [$i = 1, \ldots, k(G)$]. The chromatic information index has been introduced:[58]

$$\bar{I}_{chr} = \min_{V} \left\{ -\sum_{i=1}^{k(G)} \frac{n_i(V)}{n} \log_2 \frac{n_i(V)}{n} \right\}$$

and $\bar{I}_{chr}$ and $\bar{I}_{orb}$ have been compared. In particular, it has been shown that, for monocyclic structures of any size, $\bar{I}_{orb} = 0$, since all the vertices belong to the same orbit of the group of automorphisms of the graph, but $\bar{I}_{chr} \neq 0$ for such graphs. However, for certain molecular graphs, $\bar{I}_{chr} = \bar{I}_{orb}$. The chromatic index can be determined analogously also for the edges. Chromatic information indices have been used in the analysis of the properties of alternant hydrocarbons. The conditions for the existence of the Kekulé structure of aromatic hydrocarbons have been formulated in terms of the chromatic indices.[14]

(d) The matrices of the graph and information indices. The set of the elements of the adjoint matrix A of order n, whose elements are zero or one, can be subdivided into two classes consisting respectively of zeros and ones. If n_1 and n_2 are the numbers of elements in these classes and $n^2 = n_1 + n_2$, then the quantity

$$\bar{I}_A = -\sum_{i=1}^{2} \frac{n_i}{n^2} \log_2 \frac{n_i}{n^2}$$

characterises the inhomogeneity of the composition of the set of the elements of the matrix A. The information indices can be constructed analogously for the edge adjacency matrix, the cycle matrix, the incidence matrix, etc.[14,59] Information indices have been used in a number of studies to analyse the structure of IS consisting of the degrees of the vertices $\{v_i\}$ or the distance degrees of the vertices $\{d_i\}$. Any two elements having equal values were assigned to the same class. The information indices corresponding to these subdivisions were denoted by ${}^{V}I_A^E$ and ${}^{V}I_D^E$ respectively. The information index I_{conn},[59] defined on the bases of the edge adjacency matrix, can be constructed analogously: the non-zero elements of the matrix are subdivided, for example, into the orbits of the group of automorphisms of the matrix. If $n_{c,i}$ is the number of elements in the ith orbit and n_c the total number of non-zero elements in the matrix, then

$$\bar{I}_{conn} = -\sum_{i} \frac{n_{c,i}}{n_c} \log_2 \frac{n_{c,i}}{n_c} .$$

(e) The use of compound topological indices for the construction of TI of the information type. Some of the topological indices considered above are represented by the sum of local or integral TI. Such indices can be conveniently referred to as compound. For example, the Wiener (W), Hosoya (Z), and the Randić (χ) indices as well as the Balaban centric index B are compound. New indices of the information type have been derived in a series of studies on the basis of these TI. In their construction, the set of components whose sum yields the initial TI was subdivided into classes in some way. For example, the Wiener index W, which can be written in two equivalent forms, i.e.

$$W = \sum_i i g_i = \frac{1}{2} \sum_{i,j} d_{ij},$$

has been used to construct the indices I_D^W, $\bar{I}_D^W$, I_D^E, $\bar{I}_D^E$, I_D^M, and $\bar{I}_D^M$, which are defined by the following formulae:[14,16,19]

$$I_D^W = W \log_2 W - \sum_j g_j j \log_2 j; \quad \bar{I}_D^W = -\sum_j g_j \frac{j}{W} \log_2 \frac{j}{W};$$

$$I_D^E = \frac{n(n-1)}{2} \log_2 \frac{n(n-1)}{2} - \sum_i g_i \log_2 i;$$

$$\bar{I}_D^E = -\sum_j \frac{2g_j}{n(n-1)} \log_2 \frac{2g_j}{n(n-1)};$$

$$I_D^M = 2W \log_2 2W - \sum_i d_i \log_2 d_i;$$

$$\bar{I}_D^M = -\sum_i \frac{d_i}{2W} \log_2 \frac{d_i}{2W} .$$

In these formulae, g_j is the number of pairs of MG vertices at a distance j and d_i the distance degree of the ith vertex. Analogous expressions have been constructed also for the indices B, Z, and χ, for example:[16]

$$\bar{I}^Z = -\sum_k \frac{p(G,k)}{Z} \log_2 \frac{p(G,k)}{Z} .$$

(f) Information indices and long range effects. As stated in subsection 3 of this Section, TI which depend on the structure of different coordination spheres of the MG vertices (for example, the indices K_l for $l = 2,3$) are used in theoretical chemistry. In this subsection we shall consider a series of information-theoretic indices of analogous types. The definition of these TI is based on the subdivision of the set of graph vertices into equivalent classes, in which the character of the immediate environment of the vertices, including their degree and the multiplicity of the corresponding edges, is taken into account in detail.

Two vertices i and j belong to the same class if, firstly, they correspond to atoms of the same type and have equal degrees; secondly, each of these vertices has the same number of first neighbours $i_1, \ldots, i_m$ and $j_1, \ldots, j_m$; thirdly, there exists a mutually unambiguous mapping of the set of vertices $i_1, \ldots, i_m$ on the set of vertices $j_1, \ldots, j_m$, $i_\alpha \leftrightarrow j_\beta$, for which the vertices i_α and i_β correspond to atoms of the same type; fourthly, the orders of the vertices i_α and j_β are identical, i.e. $\nu_{i_\alpha} = \nu_{j_\beta}$; fifthly, the multiplicities of the edges (i, i_α) and (j, j_β) are identical. Only TI of information-theoretic type have been compared with this type of sub-division of the vertices of the molecular graph into equivalence classes:[60-72] ${}^1IC$ (Information Content), ${}^1SIC$ (Structural Information Content), ${}^1CIC$ (Complementary Information Content), and ${}^1BIC$ (Bonding Information Content), which are defined by the formulae

$${}^1IC = -\sum_i \frac{n_i}{n} \log_2 \frac{n_i}{n}; \quad {}^1SIC = \frac{{}^1IC}{\log_2 n};$$

$${}^1CIC = \log_2 n - {}^1IC; \quad {}^1BIC = {}^1IC/\log_2 q .$$

In these formulae, n is the number of graph vertices, n_i the number of vertices in the ith equivalence class, and q the number of graph edges. The index ${}^1CIC$ characterises the deviation of the topological index ${}^1IC$ from its maximum value ${}^1IC_{max} = \log_2 n$. The differences between other coordination

spheres can be taken into account analogously, which leads to the indices ${}^{k}IC$, ${}^{k}CIC$, ${}^{k}SIC$, and ${}^{k}BIC$;[64] the symbol k characterises the order of the coordination sphere.

Together with the information topological indices ${}^{k}IC$, etc. mentioned above, use is also made of "weighted" information indices[73] based on the subdivision of the graph vertices into the equivalence classes described above. However, in this case a weighting factor equal to the van der Waals volume of the corresponding atom is attributed to each vertex and then the weighting factors of the vertices referring to the same class are added together and the index

$$ {}^{k}IC_v = -\sum_{i=1}^{j} \frac{v_{is}}{v_s} \log_2 \frac{v_{is}}{v_s} \text{ and } v_s = \sum_{i=1}^{j} v_{is} , $$

where v_{is} is the sum of the weighting factors of the vertices of the ith class and j is the number of classes, is calculated. The topological indices ${}^{k}SIC_v$, ${}^{k}BIC_v$, and ${}^{k}CIC_v$ are determined analogously.

We may indicate yet another information index I_{sym}, which is used to characterise the molecular structure but is not topological in the generally accepted sense. The definition is based on allowance for the molecular symmetry and has been proposed in a study[74] where the following criterion of the equivalence of atoms was introduced: the atoms are assumed to be equivalent if they are interconverted by some kind of operation involving the symmetry point group of the molecule.

6. Other Topological Indices

The adjoint matrix of the graph $A = (a_{ij})$ can be used to construct certain other matrices, which are useful in finding new IS and hence also other TI. For example, in the method of potentials, which is used to establish the isomorphism of graphs,[40] the matrices $L = (l_{ij})$ and $H(h_{ij})$, where $l_{ij} = -a_{ij}, (i \neq j)$, $l_{ii} = \nu_i + 1$, and $H = L^{-1}$, are defined. The matrix $D^H = (d_{ij}^H)$ with the elements $d_{ij}^H = 0.5(h_{ii} + h_{jj}) - h_{ij}$ has been introduced.[39] The matrices L, H, and D^H have been used to define new topological indices:

$$ \prod_{i \neq j} d_{ij}^H, \det L, \det H. $$

We may mention several further graph invariants, which are discussed in the mathematical literature[11,23] but which have not so far found application in theoretical chemistry as TI: the numbers of the vertex and edge coverings, the vertex and edge independence numbers, thickness, edge connectivity, deformability, and certain others. In conclusion we may note one other TI for simple graphs, which is known as the minimum binary code.[33] For its construction, each adjoint matrix of the graph is formulated and a single row of length n^2 made up of zeros and ones. Each such row can be regarded as the binary formulation of a certain number. The smallest of all these numbers, corresponding to the adjoint matrices, is in fact referred to as the minimum binary code. We may note that the calculation of such a code for large matrices is fairly laborious.

7. Relation between the Topological Indices and Their Comparison

As shown above, hitherto numerous TI of different kinds have been defined. Most of them have found application in the analysis of molecular structure and in the construction of correlations between structure and property. Some of these TI are linked by simple relations. The examples of such functional relations have been discussed above. Undiscovered relations of some kind probably exist also in many other cases. The results of testing the approximate equalities of the type $T_i = a + bT_j$ for certain pairs of topological indices T_i and T_j have been reported.[75] The constants a and b were fitted by the method of least squares. Such analysis has been carried out for TI of three series of hydrocarbons—alkanes, polyalkylbenzenes, and monocyclic structures. It has been shown[75] that approximate linear relations with a fairly high correlation coefficient r ($0.84 \leq r \leq 0.99$) exist between the indices W, Z, χ, N_2, λ_1, and M_1. On the basis of such an investigation, one can postulate that the indices of one group carry approximately the same information about the structure of compounds of the given classes.

Certain indices, for example, I_D^W and I^Z, can be fitted by second degree polynomials in terms of Hosoya (Z) and Wiener (W) indices as well as other TI.[76]

We shall now proceed to the estimation of the quality of the TI. In coding chemical structures with the aid of TI, it is desirable that different structures should receive different index codes. However, one cannot establish a mutually unambiguous correspondence between the set of square symmetrical matrices, describing the topology of the molecule, and the set of real numbers. It is therefore always possible to select two different structures having the same values of the TI. Consequently, any TI is degenerate with respect to structures of some kind. Topological indices are usually compared in terms of their capacity to "differentiate" compounds of a certain class, i.e. in terms of the degree of their degeneracy. TI are usually employed to differentiate isomeric compounds. For example, the Balaban index $J(G)$[13] is subject to a comparatively small degree of degeneracy. Such degeneracy appears for alkane isomers only in molecules where the number of carbon atoms is greater than 20. In order to obtain TI with a smaller degree of degeneracy, superindices, equal to the sum of simpler TI, or multi-indices, which constitute an ordered sequence of topological indices, are used.[14,47] The question of the degeneracy of different TI has also been discussed in a number of publications.[13,16,77–80]

The effectiveness of 19 TI, used to identify chemical structures, has been investigated.[81] The quantity $e = n/N - t/T$, where n is the number of different values of the index in an assembly of N structures and t and T are the average time of the calculation of the index and the time required to test the isomorphism criterion respectively, has been used as a characteristic of the effectiveness of the TI. Indices defined in the method of potentials[39] and the Randić index[33] have been recognised as the most effective. One TI is regarded as "better" than another (in the estimation of the given physical property) if the correlation equation obtained with its aid is more accurate.

8. Topological Indices as Characteristics of the Shape and Size of Molecules

It has been suggested that certain TI be used to characterise the degree of branching and the shape of molecules.[19] According to intuitive ideas about the degree of branching for a specified number of vertices, the chain and star graphs have the least and most branched structures respectively. In terms of the degree of branching, the remaining structures occupy an intermediate position between them. Certain indices considered above, for example W, χ, B'', λ_1, and ${}^{2}\kappa$ have the property involving their assumption of the smallest (or greatest) value for the chain and of the greatest (or smallest) value for the star.# It has therefore been

#See also L.B.Kier, Quant.Struct.-Act.Relat., 1987, 6, 8.

suggested that they be regarded as measures of the branching of the structure. Another piece of evidence in support of the selection of these branching characteristics is the existence for a number of TI of relations of the type

$$T_j = a + bn + cn_1 + dn_2 \text{ [75]},$$

where n_1 is the number of branching points, n_2 the number of side chains connected to the main chain, and a, b, c, and d are constants.

Topological indices also vary in parallel with molecular size. It has been noted that,[82] for a series of compounds, the van der Waals volume of the molecule varies linearly with molecular refraction (MR) and determines the value of the latter to the extent of 90%. Correlations have been found[82] between MR and TI, i.e. relations of the type $R = a + bT_j$, for 17 TI and it has been concluded that the van der Waals volume can be estimated fairly accurately with the aid of the indices W and M_2 and the two information indices I_D^E and I_D^W.[83]

III. THE USE OF TOPOLOGICAL INDICES FOR THE ESTIMATION OF PHYSICOCHEMICAL PROPERTIES OF COMPOUNDS

The traditional methods for the estimation of physicochemical properties of compounds are based on additive schemes. In the classical theory of chemical structures, it is postulated that certain physicochemical properties of organic compounds (for example, the heat of formation, the boiling point, the polarisability, the dipole moment, etc.) can be calculated as the sum of the contributions ε_i, ε_{ij}, and ε'_{kl}, corresponding to the effective atoms i, the bonds (i, j), and pairs of valence- non-bonded atoms (k, l) of the corresponding molecules.[4] In the simplest case, this approach presupposes a fairly detailed classification of the vertices and edges of the MG and is based on the hypothesis that the contributions ε_x for fragments x of one type are independent of the choice of the molecule of the class under consideration.

This additive scheme for the calculation of molecular properties permits a series of modifications. Thus, one of the versions of additive schemes reduces to the representation of the numerical value y of the given property of a chemical compound by the linear function

$$y = \sum_i a_i k_i,$$

defined on the basis of the corresponding MG. In this formula, the index i characterises a MG fragment of a specific type, which can have a fairly complex structure, k_i is the topological index equal to the number of such fragments, and a_i is the contribution by each fragment of the ith class to the given property; the numbers a_i are independent of the choice of compounds. As an example, we may point out that the heats of formation of alkanes ΔH^0_{298} can be calculated approximately from the formula

$$\Delta H^0_{298}, \text{ (kcal mol}^{-1}) = 16.625 + 4.158N_1 + 1.074N_2 - 0.431N_3,$$

where N_i is the number of paths of lengths i on the MG corresponding to the carbon skeleton of the molecule.[8]

We shall now discuss the results of other studies in which different modifications of the simple additive model have been realised. In most of them, the physicochemical properties of alkanes are discussed. We may note that certain properties of hydrocarbons are satisfactorily correlated with the number of carbon atoms.[84-89] Thus the heats of atomisation and molar refractions of normal alkanes vary linearly and the boiling point and density vary non-linearly with the number of carbon atoms. However, the properties of branched hydrocarbons can no longer be described in terms of the single parameter n, since in this case the degree of branching of the molecule also plays a significant role.[10]§ Wiener has suggested in a number of studies[20,90-93] that properties of alkane isomers such as molar refraction, molar volume, the boiling point, the heat of formation, etc. be described with the aid of equations of the type

$$y - y_0 = a(W - W_0) + b(p - p_0),$$

where y is the numerical value of the given property, W the Wiener index for the MG corresponding to the carbon skeleton of the molecule, p, g_3 the so called polarity number, y_0, w_0, and p_0 are the corresponding characteristics for a normal alkane, and a and b are constants which depend on the property investigated. The value of the index W is interpreted as a quantity characterising the degree of branching of the isomer. For example, the following formula has been obtained[20] for the boiling points of alkanes t:

$$t - t_0, ^\circ\text{C} = \frac{98(W - W_0)}{n^3} + 5.5(p - p_0),$$

where

$$t_0 = 745.42 \log(n + 4.4) - 689.4; \; W_0 = \frac{1}{6}(n^3 - n); \; p_0 = n - 3,.$$

The correlations of the type described above have been analysed,[32] which has led to a conclusion concerning the cases where such indices can be usefully employed. Thus it has been shown that the heat of formation and molar refraction are best described in terms of the invariants f and p (f is the Platt index) and the heat of evaporation, the boiling point, and the molar volume can be most usefully described in terms of the indices p and W. The heats of formation of alkanes are most accurately described by a three-parameter correlation with the indices p, W, and f. Subsequently the Wiener index was used to estimate the properties of other hydrocarbons also. Relations between the Wiener index, on the one hand, and the boiling and melting points, surface tensions, viscosities, densities, and refractions of alkanes, alkynes and alkenes, as well as the boiling points of arenes, on the other have been published.[18,21] The index W has found applications also in other branches of physical chemistry: for the estimation of the width of the forbidden gap in the π-electronic spectra of conjugated micromolecules,[94,95,96] in chromatography,[94,97,98] and in crystal theory.[99,100]

In a number of studies, the Hosoya index has been used to estimate the thermochemical properties of hydrocarbons of this type.[46-48] A linear correlation between the boiling points of alkanes and both the index Z and the index

$$P = \prod_i v_i \text{ [31]}.$$

has been reported.[31] The index Z has also been used to estimate the bond orders and π-electron energies in conjugated hydrocarbons.[101,102]

It has been shown that the octane numbers of acyclic hydrocarbons can be estimated fairly satisfactorily in terms of the centric indices B, B', and B'' (especially the binormalised index B'').[103] The introduction of an additional parameter—the number of carbon atoms or the molecular weight of alkanes—increases the accuracy of the estimate.

Among other TI used to estimate the physicochemical properties of compounds, the connectivity index $^1\chi$ and its varieties, especially $^2\chi$, $^1\chi^v$, and $^2\chi^v$, have enjoyed the greatest popularity. Relations have been obtained[9,10,33,104,105]

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§ See also J.S.Chickos, R.Annuziata, L.H.Ladon, et al., J.Org.Chem., 1986, 51, 4311.

between these quantities and various physicochemical properties. We shall quote several examples of such equations. It has been shown [33] that the heat of formation of alkanes ΔH_f^0 can be described approximately by the formula

$$\Delta H_f^0 \text{ (kcal mol}^{-1}) = 12\chi - 11n - 9,$$

where n is the number of carbon atoms in the molecule. An equation relating the heats of atomisation of monohydric alcohols ΔH_a to the connectivity index χ and the number of non-hydrogen atoms n has been published:[10]

$$\Delta H_a \text{ (kcal mol}^{-1}) = -21.926 + 22.275\Delta\chi + 559.975\chi_n,$$
$$(r > 0.9999;\ s = 1.01;\ N = 19)$$

where $\Delta\chi = \chi - \chi_n$ and $\chi_n = 0.5(n-3) + 2^{1/2}$ is the connectivity index for a normal alcohol. It has been noted that the separation of the contributions by the group OH and the carbon skeleton to χ, i.e. the use of two independent parameters χ^{OH} and χ^{C} instead of the sum χ, reduces the standard error s by 30–40%. The density d of carboxylic acids can be estimated in terms of the parameters $1/\chi$ and $^3\chi$ by means of the formula[10]

$$d(\text{g cm}^{-3}) = 0.7546 + 0.4358\chi^{-1} + 0.0252^3\chi \quad (r = 0.983;\ s = 0.014;\ N = 20).$$

Table 1. Correlations between physicochemical properties and connectivity indices. [9]

Class of compounds	N	r	Refs.
Solubility in water			
Alcohols	51	0.978	[110]
Ditto	48	0.988	[37]
Ditto	51	0.965	[111]
Alkanes	18	0.958	[110]
Alkylbenzenes	13	0.989	[10]
Esters	38	0.990	[35]
Ethers	22	0.989	[10]
Boiling point			
Alcohols	63	0.970	[110]
Ditto	48	0.993	[37]
Ditto	28	0.999	[10]
Alkanes	51	0.997	[10]
Primary amines	12	0.999	[10]
Secondary amines	13	0.999	[10]
Tertiary amines	4	0.997	[10]
Alkyl halides	24	0.992	[37]
Ethers	11	0.988	[10]
Polyols	9	0.995	[37]
Carboxylic acids	22	0.996	[112]
Surface area of the molecule			
Alkanes and alcohols	69	0.978	[34]
Density			
Liquid aliphatic hydrocarbons	82	0.989	[113]
Hydrocarbons	13	0.910	[10]
Aliphatic alcohols	42	0.931	[113]
Aliphatic acids	20	0.983	[113]
Aliphatic ethers	13	0.910	[10]
Diamagnetic susceptibility			
Hydrocarbons	27	0.999	[10]
Alcohols	15	0.999	[10]
Excluded volume			
Binary mixture of n-alkanes	—	—	[114]
Heat of atomisation			
Alkanes	44	0.999	[10]
Alcohols	19	0.999	[10]
Ethers	12	0.999	[10]
Olefins	37	0.999	[10]
Thiols	14	0.999	[10]
Heat of formation			
Alkanes	67	0.999	[10]
Alcohols	20	0.998	[10]
Heat of evaporation			
Alkanes	44	0.999	[10]
Alcohols	20	0.998	[10]

Table 1 continued.

Class of compounds	N	r	Refs.
Molar refraction			
Alcohols	31	0.998	[10]
Alkanes	46	0.999	[10]
Amines	22	0.988	[10]
Alkylbenzenes	70	0.999	[10]
Ethers	9	0.999	[10]
Mixed group of compounds	65	0.990	[10]
Olefins	39	0.999	[10]
Phenyl-substituted compounds	25	0.990	[37]
Molar volume			
n-Alkanes at 20 °C	14	0.999	[114]
n-Alkanes at 50 °C	13	0.999	[114]
n-Alkanes at 100 °C	15	0.999	[114]
Polarisability			
Mixed group of compounds	36	0.990	[34]
Partition coefficient between water and 1-octanol			
Alcohols	49	0.997	[115]
"	14	0.999	[116]
Amines	12	0.998	[116]
"	28	0.979	[115]
Carboxylic acids	9	0.996	[115]
Hydrocarbons	45	0.975	[115]
Esters	24	0.999	[115]
Ethers	12	0.976	[115]
Ketones	16	0.993	[115]
Phenols	16	0.988	[116]
Mixed group of compounds	66	0.970	[116]
Ditto	138	0.986	[115]
Gas chromatographic retention indices on squalane			
Alcohols	—	0.994	[118]
Esters	—	0.991	[118]
Ethers	—	0.968	[118]
Ketones	—	0.996	[118]
Van der Waals constant b			
Mixed group of compounds	20	0.981	[37]
Positronium annihilation cross-sectional area			
Benzene and its derivatives	17	0.997	[117]
Alkanes	47	0.999	[117]
Halogeno-compounds	31	0.998	[117]
Oxygen-containing compounds	46	0.998	[117]
Unsaturated compounds	33	0.984	[117]
Mixed group of compounds	182	0.996	[117]

Notation. N is the number of compounds and r the correlation coefficient.

The topological index χ proved to be useful in chromatography for the estimation of retention indices.[104,105] However, in this case, together with χ, it is necessary to use also other topological characteristics of the molecule, describing its size, for example, the number of paths of length 3 or the number of six-membered rings in aromatic hydrocarbons.[104]

We shall now proceed to information TI. It has been shown that the Morowitz index I_{MOR} is correlated with the entropies and heats of formation of organic compounds of different classes.[14,106] Equations of the type

$$y = a + bn + cI_D^W + dI_D^W n,$$

where a, b, c, and d are constants, have been used to estimate the molecular volumes and properties of hydrocarbons such as heats of formation, oxidation, and evaporation and the boiling points.[16,94,107] A relation between the index I_D^W for alkylbenzenes and their chromatographic retention parameters has also been reported. Analogous relations have been obtained likewise for the index I_D^E in the case of o-dialkylbenzenes and isoalkanes.[108] The index I_D^M has found an application in the estimation of different thermochemical properties of alkylbenzenes.[109] There is an equation[14] relating the heat of evaporation ΔL_{298} of alcohols and the index I_{orb}:

$$\Delta L_{298} \text{ (kcal mol}^{-1}) = 0.265 I_{orb} + 8.566 \quad (r = 0.989;\ s = 0.414;\ N = 15).$$

A linear relation has been established between the entropies of alkanes, alkenes, alcohols, and organic acids and the information index I_{sym}.[74] Other examples of the use of information topological indices have been discussed in a monograph.[14]

Table 1 summarises data on some of the relations described in the literature between the connectivity indices and various physicochemical properties.

IV. TOPOLOGICAL INDICES AND BIOLOGICAL ACTIVITY

One of the most important applications of TI involves their use to establish quantitative relations between the structure and biological activity of molecules. Biological activity is usually estimated in terms of the molar concentration of the substance necessary to attain a specified level of biological activity. Various parameters are used as characteristics of biological activity, including LD_{50} (or LC_{50}), representing the dose which destroys 50% of the organisms tested, the dose ED_{50} of the antagonist which lowers by 50% the effect of the standard dose of the agonist, the concentration *MIC* of the inhibitor which suppresses the growth of the experimental biological object to a minimal level, the molar concentration I_{50} of the inhibitor which reduces the rate of the enzyme-catalysed reaction by a factor of two, etc.[12] The hydrophobicity parameter lg *P* (*P* is the partition coefficient of the given compound between water and a lipid-simulating phase, usually 1-octanol) as well as the Hammett and Taft constants, reflecting the electronic and steric structures, are most often used as empirical parameters in the study of the relation between structure and activity. An extensive bibliography on the methods used to establish a relation between structure and biological activity has been published[12,40,119] and the principal molecular characteristics used to solve this problem have been described.

Among the TI used to investigate biological activity, the molecular connectivity indices, especially the Randić index χ, have found the most extensive applications. We shall consider certain examples of the use of indices of this type.

A correlation between lg *MBC* and the index χ has been found by Kier et al.[34] from the results of Agin et al.[120] for a series of anaesthetics (aliphatic alcohols, ketones, ethers, amines, phenols, heterocycles, and hydrocarbons):

$$\lg MBC = 3.55 - 0.762\chi \quad (r = 0.983;\ s = 0.390;\ N = 36).$$

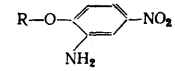
Here *MBC* is the minimum blocking concentration of the anaesthetics for isolated muscle or nerve fibres. We may note that a relation between lg *MBC* and the polarisability α has been discovered for the given group of compounds[120] and a correlation has been found[34] between α and χ. These facts have served as the basis of the above equation relating lg *MBC* and χ.

Certain relations between the index χ and biological activity have been discussed.[115,121,122] The discovery of linear correlations between χ and lg *P* and also between lg *P* and the biological activity of aliphatic alcohols made it possible to establish a linear relation between χ and biological activity.[115] The narcotic effect of alcohols on the larvae of certain crustaceans and the inhibition of the movement of tadpoles have been considered as a manifestation of the biological activity of such substances. For aliphatic alcohols, ethers, esters, ketones, and carbamates, relations have been found between the index χ and the non-specific narcotic activities of the above compounds on tadpoles ($N = 36$).[121] The dependence of the non-specific toxic activity of monofunctional alcohols, ethers, and ketones on fungi of a particular species and the index χ ($N = 45$) was considered in the same study. A linear correlation has also been reported[121] between the index χ for a series of compounds and the inhibition of the enzymes succinate oxidase, thymidine phosphorylase, and butyrylcholinesterase. Thus an equation of the following type has been obtained for a series of saturated and unsaturated aliphatic alcohols, ketones, phenols, aniline, and pyridine, which inhibit succinate oxidase:

$$-\lg I_{50} = 0.916\chi - 1.582 \quad (r = 0.966;\ s = 0.169;\ N = 13).$$

Quadratic correlations between lg I_{50}, lg LC_{50}, and quantities such as lg *P* and χ have also been described. Such correlations have been observed, for example, in estimations of the bactericidal activities of alkylbenzylmethylammonium salts and of the narcotic activities of 5,5-dialkylbarbituric acids on certain animal species.[16,63,122]

Correlations between the connectivity indices and parameter of types of biological activity such as non-specific narcotic activity, enzyme inhibition, bactericidal activity, toxicity, and anaesthesising activity have been examined in a monograph.[10] The possibility of estimating the taste and smell of substances with the aid of topological characteristics of molecular structure has been discussed in the same publication. Thus the relative sweetness *RS* of nitroanilines of the type



is expressed in terms of the parameters $^1\chi$ and $^1\chi^v$ in the following manner:

$$\lg RS = 0.350\,{}^1\chi + 0.694\,{}^1\chi^v - 3.856 \quad (r = 0.953;\ s = 0.222;\ N = 9).$$

According to one of the theories of smell, the smell of a substance is determined by the shape and size of its molecule.[12] It has been suggested[10] that molecular shape be characterised by the parameter χ/n and the hypothesis was put forward that substances having identical smells should have similar values of χ/n. To confirm this hypothesis, a list of structurally different substances having the almond smell and similar values of χ/n is quoted.[10]

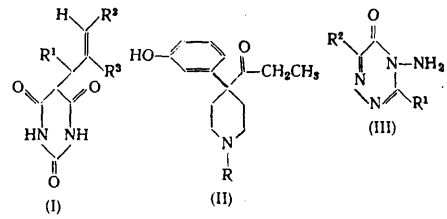
Together with the first-order connectivity index, higher-order connectivity indices have been considered in a number of studies.[10,123] For example, the topological index $^2\chi^v$, calculated for phenol derivatives, has been used to analyse their antifungal activity characterised by the parameter *MIC*.

We shall now consider other topological indices. A series of correlations between the indices I_{orb} and I_{sym}, on the one hand, and the inhibition of enzymes, alcohols, and their non-specific narcotic activity and toxicity, on the other, has been discussed in a monograph.[14]

Systematic studies on the "structure–biological activity" problem, based on the information indices *IC*, *SIC*, *BIC*, and *CIC*, have been carried out.[60–73,124] The relation between the structure and toxicity of ethers, characterised by the parameter LD_{50}, has been analysed.[60] The quantities $^1\chi$, $^1\chi^v$, χ^v, *W*, *IC*, *SIC*, *CIC*, I_D^W, and $\bar{I}_D^W$ were used as the TI and it was established that the most suitable structural characteristic among those quoted is the index $^1\chi^v$ in this instance. A correlation equation of the following type has been obtained in terms of the TI:

$$\lg LD_{50} = -0.7207\,{}^1\chi^v - 1.3868 \quad (r = 0.938;\ s = 0.246;\ N = 15).$$

The indices *IC*, *CIC*, $^1\chi$, $^1\chi^v$, I_D^W, $\bar{I}_D^W$, and *W* as well as the parameters lg *P* and the van der Waals volume V_W have been used as structural characteristics to estimate the anaesthesising activities of barbiturates.[61] Four groups of biologically active molecules have been investigated by Basak et al.:[63] alcohols (toxicity); barbiturates (anaesthetic (I); ketobemidones (analgesics) (II), and triazinones (herbicides) (III). There were all characterised with the aid of the indices *W*, *IC*, *SIC*, *CIC*, I_D^W, $\bar{I}_D^W$, $^1\chi$, and $^1\chi^v$.



(I) (R^1,R^2,R^3 = alkyl groups)

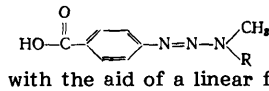
(II) [$R = CH_3(CH_2)_n$, where $n = 0, ..., 9$]

(III) ($R^1 = SCH_3$; R^2 = alkyl groups)

It was established that the most convenient structural characteristics in such cases are the indices CIC and $\bar{I}_D^W$ and the most suitable type of functional relation is quadratic.

The indices IC, SIC, and CIC are used to characterise derivatives of piperidine (inhibition of butyrylcholinesterase), barbiturates (hyponotic activity), alkanes (toxicity), aliphatic alcohols (local anaesthesia, narcotic effect on crustacean larvae), and a mixed group of compounds which are tranquillizers.[66-68]

The antitumour activity of triazenes of the type



has been estimated with the aid of a linear function of two variables lg P and ^2BIC.[124] The same type of biological activity has been considered in a study[69] where a wider set of parameters was used, namely lg P, V_W, IC, and SIC. The index SIC is also useful in the analysis of the biological activity of triazinones (herbicides) and N-alkylnorketobemidones (analgesics).[70] The higher-order indices ^kCIC, ^kIC, and ^kSIC, where $k > 1$, have been used[64] to analyse the biological activity and structures of a series of organic compounds. In particular, correlations of the type lg $LD_{50} = ay^2 + by + c$ between the toxicity of barbiturates (LD_{50}) and characteristics such as lg P, W, I_D^W, $\bar{I}_D^W$, $^1\chi^v$, ^2SIC, ^2CIC, and $^1\chi\lambda$ have been described. The most accurate correlation has been obtained using the indices ^2SIC and ^2CIC.

In some of the studies enumerated above, it is emphasised that the use of TI as structural parameters instead of characteristics such as lg P leads to more accurate correlations. The presence of several correlations, obtained in terms of different structural parameters, for the same property makes it possible to identify those which are most significant for the given property. Hypotheses concerning the mechanism of the action of active compounds can be constructed on the basis of such analysis.

The application of the index $^2\kappa$ (see above) in the quantitative estimation of the properties of chemical compounds has been discussed.[142] For example, it has been suggested that the index $^2\kappa$ be used as the characteristic of the molecular shape; it has been shown that, for similar values of $^2\kappa$ (i.e. for similar shapes), the substances have similar smells. A relation has been established between $^2\kappa$ and the bactericidal activity of phenol derivatives with halogenoalkyl substituents:

$$\lg PC = 1.817\,{}^2\kappa - 0.131\,({}^2\kappa)^2 - 2.899 \quad (r = 0.955;\ s = 0.27;\ N = 49),$$

where PC is the minimum concentration of the substance inducing specified biological effects in 10 min. The index $^2\kappa$ has also been used[142] to estimate the sweetness of nitro- and cyano-anilines.

Together with the TI mentioned in this Section, a series of topological indices, originating from the study of the electronic structures and chemical reactivities of biologically active compounds with the aid of topological approximations of quantum chemistry, have also been used in estimating biological activities. This field developed most vigorously in the 1960's and it has been described in detail in a monograph.[125]

V. QUANTUM-CHEMICAL METHODS AS A SOURCE OF TOPOLOGICAL INDICES

1. The Hückel Method and Graph Theory

In the examples considered previously, the TI arose as a rule as a result of the formal analysis of the structure of the molecular graph. Such analysis was supplemented in many instances by qualitative considerations concerning the choice of criteria for the estimation of the degree of branching or compactness of the molecule. In this Section, we shall discuss TI which appear naturally within the framework of certain mathematical models used to investigate the electronic structures of molecules. We shall follow in relation to one such model how the solution of the problem of the electronic structures of conjugated molecules reduces to the analysis of the TI of certain MG.

A molecule with a system of conjugated double or triple bonds contains as a rule a fairly extended planar fragment, which makes it possible to sub-divide the electronic system into two parts—the σ- and π-components—and to investigate each system independently.[125-128] Later we shall consider only the π-electron system assuming that it exists in a certain effective field generated by the atomic nuclei, the electron inner shells, and the σ electrons participating in the formation of localised two-centre σ-bonds. In the case of conjugated hydrocarbons, the number of π electrons is usually the same as the number of carbon atoms forming the conjugated part of the molecule. The structure of the conjugated part can be described by a molecular graph in a simplified form. It is obtained from the complete MG by removing the vertices corresponding to univalent substituents.

The properties of a system incorporating m π electrons are known[125-128] to be described in terms of one-electron energy levels ε_k and the corresponding molecular orbitals

$$\psi_k(r) = \sum_{j=1}^{m} c_j^{(k)} \varphi_j(r),$$

where $\phi_j(r)$ is an atomic $2p_z$ orbital centred on the jth atom of the conjugated part of the molecule. We shall denote by $\mathbf{c}^{(k)}$ the unit vector with the components $c_1^{(k)}, ..., c_m^{(k)}$. Then, in the case of hydrocarbon systems, the vectors $\mathbf{c}^{(k)}$ and one electron energy levels are found by solving the system of equations $H\mathbf{c}^{(k)} = \varepsilon_k \mathbf{c}^{(k)}$, where $H = \alpha E + \beta A$, E is the mth order unit matrix, A the adjoint matrix of the MG describing the conjugated part of the molecule, and α and β are the Coulombic and resonance integrals. For heteroatomic systems, the matrix A must be replaced by the adjoint matrix of the weighted MG.

We shall denote by λ_j (where $j = 1, ..., n$) the eigenvalues of the matrix A arranged in decreasing order. The one-electron energy levels ε_j can be then represented in the form $\varepsilon_j = \alpha + \lambda_j\beta$, where $\beta < 0$. The eigen-vectors of the matrices H and A are identical. The energy of the ground state of the system with an even number of m of π electrons can be calculated in terms of λ_j by the formula

$$\varepsilon_\pi = 2\sum_{j=1}^{m/2} \varepsilon_j = m\alpha + 2\beta \sum_{j=1}^{m/2} \lambda_j .$$

The density matrix P, whose elements are

$$p_{ij} = 2\sum_{k=1}^{m/2} c_i^{(k)} c_j^{(k)},$$

is defined in order to analyse the distribution of electron density. The diagonal element p_{ii} of the matrix P is called the π-electron density at the ith atom, while the non-diagonal element p_{ij}, corresponding to atoms linked by valence bonds, is called the order of the π-bond (i,j). The elements of the matrix P are TI of the local type and in terms of these TI

the formula of the total π-electronic energy of the ground state of a conjugated system containing heteroatoms can be formulated as follows:

$$\varepsilon_\pi = \sum_i \alpha_i p_{ii} + \sum_{i \neq j} p_{ij}\beta_{ij} ,$$

where $\alpha_i = H_{ii}$ and $\beta_{ij} = H_{ij}$ are respectively the Coulombic and resonance intervals. It can be shown[127] that the elements of the matrix P characterise the response of a π-electron system to small perturbations leading to changes in one of the parameters α_i or β_{ij} and can be found as partial derivatives of ε_π with respect to the corresponding parameters α_i and β_{ij}. The use of the topological indices p_{ij} for the interpretation of data on the chemical reactivity of conjugated molecules is based on this property.[127]

In the case of hydrocarbons, the expression for the energy of the ground state ε_π includes as a rule only non-negative eigenvalues λ_j of the corresponding MG. The energy levels ε_j located below the Coulombic integral α correspond to such eigenvalues. The energy levels ε_j satisfying the inequality $\varepsilon_j < \alpha$ are called bonding.[125] The term "antibonding" is used to characterise the energy levels to which $\lambda_j < 0$ correspond. On the other hand, if $\lambda_j = 0$, then $\varepsilon_j = \alpha$; such an energy level is referred to as non-bonding. If the number of bonding orbitals is $m/2$, then it is said that the π-electron system has a closed (in the Hückel sense) electron shell.

The character of the electron shell of conjugated hydrocarbons can be interpreted in terms of the topological index $\omega = n_+(G)/m$, where $n_+(G)$ is the number of positive eigenvalues of the molecular graph G. If $\omega = 1/2$, then the molecule has a closed (in the Hückel sense) electron shell. For $\omega > 1/2$, there is a deficiency of π electrons and, when $\omega < 1/2$, there is an excess of π electrons. The presence of a closed π-electron shell in a conjugated hydrocarbon molecule is attributed to the stability of the π-electron system and the molecule as a whole.[125–127] Qualitative conclusions used[126–139] for *a priori* estimates of the possibility of the existence of chemical compounds are based on this precise hypothesis. The results of studies[135–139] where the problem of the existence of polyhedral C_n carbon clusters is discussed are based to a large extent on the criterion specifying whether or not the electron shell is closed in the Hückel sense.¶

It follows from the data described in this Section that the study of the electronic structure of conjugated systems in terms of the Hückel π-electron approximation reduces to finding a series of invariants of molecular graphs corresponding to conjugated systems. We shall indicate the most important of these quantities: the eigenvalues of the MG $\{\lambda_j\}$, the sum of the positive eigenvalues

$$\lambda_+ = \sum_{\lambda_j > 0} \lambda_j$$

the π-electronic charges on the atom p_{ii}, and the π-electron bond orders p_{ij}. A more complete list of the TI used in the Hückel method can be found in Table 2.

The TI used for the purpose of classification occupy a special place in the theory of conjugated systems. They include, for example, the conjugation energy and the topological resonance energy (TRE). The latter was introduced by Aihara[140] and Gutman et al.[141] and has been used to estimate the relative stabilities and degrees of aromaticity of conjugated molecules. The topological resonance energy is determined in terms of the zero values of the so called acyclic polynomial in the construction of which use is made of the combinatorial properties of the coefficients a_j characterising the polynomial $P(G,x)$ of the molecular graph G. It can be shown[23] that each coefficient a_j represents the sum of the contributions corresponding to special subgraphs of the graph G. Among the subgraphs, there are those which contain cyclic components. We shall denote by a_j' the sum of the contributions introduced into the expression for a_j solely by the subgraphs which do not contain cyclic components. The polynomial $P(G,x)$ with the coefficients a_j' is called acyclic.[141] It has only real roots and is regarded as the characteristic polynomial of the hypothetical π-electron system with the same number of π electrons as in the initial system. The difference between the energies of the ground states of these two systems is called the topological resonance energy. These questions are discussed in greater detail in the review of Graovac et al.[142] Certain new TI used to estimate the degrees of aromaticity[144,145] have been compared.[143]

Table 2. Certain topological indices used in the Hückel method.[126]

Topological index ($m = 2k$)	Name	Application
$\lambda_1, \ldots, \lambda_m$	Eigenvalues of the MG adjacency matrix	Calculation of one-electron energy levels $E_i = \alpha + \beta\lambda_i$; interpretation of photoelectron and UV spectra
$\lambda_+ = \lambda_1 + \ldots + \lambda_{m/2}$	Sum of positive eigenvalues of the MG adjacency matrix	Calculation of the energy of the ground state of the π-electron system ($E_\pi = m\alpha + 2\beta\lambda_+$); estimation of the relative stabilities of the conjugated systems; calculation of the resonance energy
$p_{ij} = 2\sum_{k=1}^{m/2} c_i^{(k)} c_j^{(k)}$	Elements of the density matrix: p_{ii} is the π-electron density at the atom i and p_{ij} at the π-electron bond order	Bond orders—estimation of bond lengths, force constants, and chemical reactivity; p_{ii} elements-estimation of the dipole moments and reactivities
$F_i = N_{\max} - \sum_{j \neq i} p_{ij}$	Free valence index	Used as the reactivity index in radical substitution reactions; $N_{\max}$ is the maximum permissible value of $\sum_{i \neq j} p_{ij}$ for atoms of the given type
$\lambda_{m/2}$, $\lambda_{m/2+1}$; $\{c_i^{(m/2)}\}$, $\{c_i^{(m/2+1)}\}$	The smallest positive and the greatest negative eigenvalues of the MG adjacency matrix and the corresponding eigenvectors	Estimation of the first ionisation potential, electron affinity, and the energy of the first electronic transition; polarography; theory of chemical reactivity

Notation: $m = 2k = N$ is the number of centres in the conjugated systems, where N is the number of π electrons; $\lambda_j \neq 0$ for $j = 1, \ldots, m$.

Various correlations between TI (of the Hückel type) and different physicochemical properties of conjugated molecules have been described fairly completely in monographs.[125–127] The usefulness of the Hückel method for the interpretation of the photoelectron spectra of polycondensed aromatic hydrocarbons has been discussed.[146] It has been shown for more than 250 compounds that the potentials of ionisation from the upper π-energy levels can be fitted with an adequate accuracy (the standard deviation does not exceed 0.1 eV) by analytical

¶ See also D.J.Klein, W.A.Seitz, and T.G.Schmalz, Nature, **1986, 323, 703.**

expressions whose form is determined by the one-electron energy levels and the bond orders.

Quantities such as the eigenvalues of the MG, the elements of the density matrix, and other characteristics of the molecular systems can be readily calculated with the aid of a computer. However, these data, many of which have been compiled in handbooks (see, for example, Streitwieser and Brauman[147]), are difficult to interpret directly in structural terms. Nevertheless such interpretation is of interest for the understanding of the sources of the appearance of definite functional relations between the structure of the molecule and its properties. The field associated with the search for relations between the results of Hückel calculations and clear characteristics of molecular graphs has therefore developed fairly vigorously in recent years.[142] For example, a complete series of approximate formulae of different degrees of complexity has been obtained for the sum of the positive eigenvalues of the MG, which, as mentioned above, is linearly related to the total π-electronic energy. A catalogue of the most convenient of these together with estimates of their accuracy has been published.[148,149] Analogous formulae have been obtained for the maximum eigenvalue and also for the difference between the smallest positive and greatest negative eigenvalues of the adjoint matrix.[150–152] The latter quantity is of interest for the estimation of the spectroscopic characteristic of conjugated molecules.

The mathematical model of the electronic structures of unsaturated molecules described in this Section can be extended also to the case where it is necessary to take into account all the valence electrons (for example, to saturated systems). One of the possible extensions has been proposed in studies[153,154] where the investigation of the electronic structure of molecules in terms of the valence approximation reduces to the analysis of the spectroscopic characteristics of weighted graphs of a special type. The vertices of these graphs correspond to different hybrid orbitals constructed from atomic functions of the *s* and *p* types.

2. Relations between Certain Topological Indices of the Quantum-Chemical Type

As mentioned above in Section II, a series of TI are linked by simple functional relations. Some of these relations are empirical and have been established by the method of least squares. Similar relations have been obtained in a number of studies[10,95,96,155–158] between certain topological indices defined in the Hückel method and indices which do not have a direct bearing on the method (such as, for example, the connectivity indices, the Wiener numbers, and others). It has been shown[155] that, for conjugated hydrocarbons, the first-order connectivity index $^1\chi^v$, determined from the formula

$$^1\chi^v = {\sum_{i,j}}' (\delta_i^v \delta_j^v)^{-1/2},$$

is fairly satisfactorily correlated with the total π-electronic energy. In this formula $\delta_i^v = z_i^v - h_i$, where z_i^v is the number of valence electrons of the *i*th atom and h_i the number of univalent substituents of the given atom. Relations of an analogous type have been established[156] between the charges on the atoms and the Mulliken bond orders obtained by the extended Hückel method for aliphatic hydrocarbons, on the one hand, and the atomic connectivity indices χ_i^v, found from the formula

$$\chi_i^v = \frac{1}{2}{\sum_{j}}' (\delta_i^v \delta_j^v)^{-1/2},$$

on the other. Such formulae are useful, since they make it possible to imitate fairly simply the results of calculations of the electronic structure of molecules by MO methods, which cannot be carried out without using modern computers.

A series of TI appear naturally when another quantum-chemical method is used—the valence bond method[159] and some of its modifications.[144,145] Methods of this type are based on the construction of a many-electron wave function in the form of a linear combination of many-electron basis functions of a special type. In the case of the π-electron approximation, where only the π orbital is taken into account for each atom, a certain spin pairing scheme for the π electrons associated with the corresponding carbon atoms corresponds to each basis function. This scheme can be described in terms of the graph theory. Only electrons corresponding to atoms linked by valence bonds are usually combined in pairs. Each such scheme is described by a Kekulé graph. It consists of a set of connected two-vertex subgraphs MG (edges), which cover the vertices of the initial graph and have no common vertices in pairs. The Kekulé graph can be related to a structural formula with single and double bonds. Suppose that an approximate wave function ψ_k corresponds to each such structural formula. Then the total wave function ψ can be formulated as the linear combination

$$\psi = \sum_k a_k \psi_k.$$

The numbers a_k are called the weighting factors of the structures and are treated as variational parameters. The procedure described above is usually employed to investigate the stability of bicyclic benzenoid hydrocarbons and their heteroanalogues. On the basis of qualitative considerations, it can be shown that, among the isomers of benzenoid hydrocarbons, the greatest stability should be shown by the isomer to which corresponds the greatest number of Kekulé structures.[159]

The following procedures are used to estimate the bond strength. The number of all the Kekulé structures is found. Then the edge, for example (i,j), corresponding to a bond C–C in the initial molecule, is selected in the MG. Next this edge together with the edges incident with it are excluded from the MG. We shall denote the number of Kekulé structures in the graph obtained in this way by k_{ij}. The ratio $\tilde{p}_{ij} = k_{ij}/k$ is called the Pauling bond order.[160,161] It has been established that, for alternative hydrocarbons not containing four-membered rings and non-bonding energy levels (which is equivalent to the validity of the inequality $\det A \neq 0$, where A is the adjoint matrix), this quantity can be calculated from the formula

$$\tilde{p}_{ij} = \sum_{\lambda_k > 0} c_i^{(k)} c_j^{(k)} / \lambda_k,$$

where $c_i^{(k)}$ are the components of the *k*th eigenvector of the adjoint matrix A. The quantity on the right-hand side was introduced by Ham and Ruedenberg[161] and is called the Ham and Ruedenberg bond order. A number of other relations between TI, used in various quantum-chemical methods, have also been discussed (see, for example, Hosoya and Hosoi[157]).

The examples presented in Sections II and V show that there are simple relations, determined ultimately by the combinatorial properties of the initial MG, between TI which are at first sight of different nature. The search for various systems of independent TI, in terms of which it would be possible to calculate any other TI, is therefore of interest. The solution of this problem would make it possible to construct various correlations more effectively and with better justification and to predict the properties of compounds which have not yet been synthesised.

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Two main aspects of the problem of topological indices can be distinguished. The first is associated with the development of effective methods for the coding of molecules, which is of great interest in connection with the use of information-search systems for different purposes. The second aspect refers directly to the search for sets of structural fragments of molecules which are responsible for the manifestation of particular physicochemical properties of concrete compounds and to the discovery of regularities in the character of their variation.

It appears at first sight surprising that the properties of a substance can be predicted with the aid of simple mathematical models of the kind described in this review. However, experience shows that the properties of many chemical compounds, whose molecules have "like" structural fragments, are indeed similar. Furthermore, one should bear min mind that, in selecting the coefficients a_i in functional relations of the type

$$y = a_0 + \sum_i a_i k_i,$$

between the numerical values of a certain property and the structural characteristics expressed in terms of TI, one takes into account implicitly not only the geometrical parameters of individual molecules (more precisely certain average characteristics) but also the features of the structure of the substance as a whole. The same property can be described in terms of different TI, which leads to unlimited possibilities for the search with the aid of computers for relations between changes in the properties of a substance and the topological characteristics of the molecular structure.† In practice, preference should be given to simpler and more accurate relations which can be used even when it has not been possible to justify reasonably the relations discovered. In his Nobel Lecture, Richard Feynman said "the only true physical description of a phenomenon involves the interpretation of the significance of the quantities in an equation from the standpoint of the experiment or, more precisely, a method of applying equations to experimental results. Once this is admitted, then the best way of creating a new theory is to guess at equations without paying attention to physical models or a physical explanation".[164] From our point of view, the method of topological indices is precisely such an approach, which makes it possible to "guess" equations relating structure to property in those fields of structural chemistry where a sufficiently reliable theory has not yet been developed or the applications of a theory encounter considerable computational difficulties.

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†Information about programs for the calculation of different TI on a computer has been published, for example, by Peredunova et al.[162] and Shtain et al.[163]

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Lanthanide Oxide Sulphides

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A systematic account is given of the methods of preparation of oxide sulphides having the composition Ln_2O_2S (where Ln = lanthanide, Sc, or Y) in the form of polycrystalline materials, single crystals, thin films, and ceramics. The crystal-chemical, thermal, thermodynamic properties of the oxide sulphides are considered.
The bibliography includes 117 references.

CONTENTS

I. Introduction 209
II. Methods of synthesis 209
III. Crystal-chemical properties 211
IV. Solid solutions in the Ln'_2O_2S-Ln''_2O_2S systems 214
V. Thermal and thermodynamic properties 215

I. INTRODUCTION

Compounds having the composition Ln_2O_2S, where Ln = lanthanide, Sc, or Y, are known for all the lanthanides without exception and also for scandium and yttrium. They occupy an intermediate position between the oxides and sulphides of the corresponding elements. All these groups of compounds are structurally related as regards either their crystal lattices or individual structural fragments. The practical aspects of the application of lanthanide oxide sulphides have attracted in the first place the continued attention of investigators and a broad spectrum of materials based on them have already been created: powders (ceramics), single crystals, thin layers, and films.

The polycrystalline oxide sulphides or solid solutions based on them, in the first place lanthanum oxide sulphide activated with Nd, Er, Tm, and Yb, are highly effective anti-Stokes phosphors (with green and blue glow) and can be used, in the form of phosphor coatings emitting in the IR part of the spectrum, to make light emitting diodes, digital and alphanumeric indicators and indicator panels, and colour television. In the USSR and other countries, methods have been developed for the growing of single crystals of lanthanum oxide sulphide activated with Nd, Er, and Yb. Combined studies on such single crystals—structural, optical, mechanical, and spectroscopic (the luminescence characteristics of laser emission)—have demonstrated their likely usefulness by the creation of low-threshold microlasers and unified light diodes. However, the difficulties in the growing of single crystals of a high quality have not as yet been overcome.

This review is devoted to the consideration of the questions concening the formation of point defects in the oxide sulphide and their thermal and thermodynamic properties, which will fill the existing gap in the literature.

II. METHODS OF SYNTHESIS

Apparently the first lanthanide oxide sulphide obtained was lanthanum oxide sulphide. Subsequently extensive patent literature appeared on the methods of synthesis of the oxide sulphides and phosphors based on them.

Studies by investigators in many countries, especially France, the USA, Finland, the USSR, etc., have been devoted to the methods of preparation of the oxide sulphides and have found extensive applications in the technology of phosphors. The methods of synthesis are distinguished by wide variety. All the known procedures reduce in essence to two schemes which are chemically fundamentally different. In the first scheme, the sulphur is introduced into the initial sulphur-free oxygen compound of the lanthanide by some kind of sulphur-containing reagent, as a rule a sulphide or elemental sulphur. In the second scheme, the initial sulphur-containing lanthanide compound is reduced, oxidised, or decomposed to the oxide sulphide. We shall consider the existing methods of synthesis of oxide sulphides in conformity with the schematic arrangement which we have proposed.

1. The Introduction of Sulphur into Lanthanide Oxide Compounds

The introduction of sulphide sulphur can be achieved by treatment with various compounds, using elemental sulphur,[1-6] hydrogen sulphide,[2,3,7-10] carbon disulphide,[11] sulphides,[5,7] ammonium or sodium thiocyanate,[5] and thioacetamide[11] (Table 1).

In the general form, the chemical reactions take place in accordance with the scheme

$$Ln_2O_3+RS\rightarrow Ln_2O_2S+RO\,,$$

where R is the group of the "sulphiding" agent. Depending on the conditions and the reagents, one of the variants of the solid-phase, liquid-phase, or gas-phase syntheses is achieved.

When elemental sulphur is used, lanthanide oxides are treated with its vapour in an inert medium in one or two stages.[1-6] In the latter case, the synthesis is carried out initially at low temperatures (400–450 °C), which is then followed by annealing at 500–800 °C (Table 1). Oxide carbonates, oxalates, formates, etc. can be used instead of the oxide.[1]

When sulphur is introduced with the aid of carbon disulphide, it is also possible to obtain oxide sulphides, but these not only contain admixtures of substances which have failed to react but are also contaminated with carbon.[11-13] The introduction of sulphur by hydrogen sulphide in a stream of argon (nitrogen) with added water vapour is carried out at higher temperatures (1100–1150 °C)[1-3,8,9] and, in the case of CeO_2, at 1300 °C.[3]

The introduction of sulphur by gaseous reagents, which takes place at the solid–gas interface, leads to the appearance of a sulphide sulphur concentration gradient in the

bulk of the oxide sulphide grain, to its non-uniform content in particles of different size, and also to the formation of non-stoichiometric phases.

Table 1. Preparation of the oxide sulphides by the "sulphiding" method.

Initial compound	"Sulphiding" agent	Side products	t °C	τ, h	Medium	Refs.
Ln_2O_3	S	Ln_xS_y	1050—1120	1—2	Ar	[1]
Ln_2O_3[a]	S (excess)	Ln_xS_y	400—450; 500—800	1—2	inert	[2—4]
$Ln_2(C_2O_4)_3$, $Ln_2O_2CO_3$	S (excess)	Ln_xS_y	700	—	inert	[1]
Y_2O_3	S (excess)	Y_xS_y	950—1000	100	inert	[5]
Eu_2O_3+EuS	S (excess)	Eu_xS_y	600	7	inert	[6]
Ln_2O_3[b]	H_2S	H_2O	1000—1100	—	Ar (95%)	[1, 2]
Ln_2O_3[c]	H_2S	H_2O	550—600	—	—	[7]
$Ln_2O_2CO_3$	H_2S	H_2O, CO_x	500—800	4—5	H_2O (5%)	[8]
Ln_2O_3	H_2S	LnS_x, H_2O	1150±10	1.5	N_2, H_2O	[9]
Ln_2O_3[d]	H_2S	H_2O, LnS_x	850—1050	12—40	—	[10]
CeO_2	H_2S	S, H_2O	1300	—	—	[3]
Ln_2O_3	CS_2	C, CO	750—800	2—8	—	[11]
La_2O_3[e]	CS_2	C, CO_x, COS, S	600	4	He	[12]
Y_2O_3	CS_2	C, CO, Y_xS_y	1000	0.5	—	[13]
Ln_2O_3[f]	$S+Na_2CO_3$	Na_2S_{2+x}, CO_2	1100	1	—	[14—19]
Ln_2O_3[g]	Na_2SO_3	Na_2SO_4	1100	1	inert	[20]
Y_2O_3	S+NaCNS	Na_2S, CO_x	750	0.5	—	[5]
Ln_2O_3	CH_3CSNH_2 (excess)	CO_x, H_2O	1200	4—6	—	[11]
Ln_2O_3	Ln_2S_3 (excess)	Ln_2S_3	1350	3	vacuum	[7, 23]
Dy_2O_3[a]	Dy_2S_3	—	1300; 1600	5 3	$p < 0.1$ Pa	[21]
Sc_2O_3	Sc_2S_3 (excess)	Sc_2S_3	1500	4	—	[24]
Y_2O_3	Y_2S_3	Y_2S_3	1000	100	vacuum	[5]

Notation: t is the temperature and τ the duration of the synthesis. [a] The synthesis is carried out in two stages. [b] The method is used in industry. [c] The temperature of the synthesis of Ce_2O_2S is 500 °C. [d] Ln = Gd—Lu or Y; the temperature and the duration of the synthesis depend on the nature of Ln. [e] The yield of the oxide sulphide is 35%. [f] The temperature of the synthesis of Lu_2O_2S is 780 °C. [g] The yields of lanthanum, praseodymium, neodymium, samarium, and europium oxide sulphides are 95—98%; Ce_2O_2S and Pm_2O_2S were not investigated.

The degree of conversion increases significantly when the synthesis is performed in the melt of the "sulphiding" agent. A mixture of the lanthanide oxide with sulphur and sodium carbonate is heated at 1100 °C.[14—19] The reaction begins with the formation of sodium polysulphides from sodium carbonate and sulphur. These polysulphides melt and then introduce the sulphur into the lanthanide oxide with formation of the oxide sulphide. An advantage of the method is the evolution of carbon dioxide on decomposition of sodium carbonate, the dioxide protecting the oxide sulphide against oxidation. The method of introducing sulphur into oxides by sodium sulphite in an inert medium is closely related to the above procedure.[20] At high temperatures, sodium sulphite disproportionates to the sulphate and the sulphide, the melt of the last compound reacting with the lanthanide oxide. The maximum yield of the oxide sulphide (88—95%) is obtained at 1100 °C, after 1 h, and for the ratio $Na_2SO_3 : Ln_2O_3 = 4 : 1$. The reactivity of the oxide in the "sulphiding" reaction depends on the position of the metal in the series of lanthanides. Manashirov and Semikhova[20] divided the oxides into three groups in terms of their reactivities: the maximum reactivity is shown by the oxides of elements ranging from lanthanum to gadolinium, which form oxide sulphides at 1100 °C; ytterbium, lutetium, cerium, and yttrium oxides, which form appreciable smounts of oxide sulphide only at 1350 °C, have been assigned to the second group; the oxides of the remaining lanthanides produce a mixture of the oxide sulphide and the oxide which failed to react at 1100 °C.

The oxide sulphides are also obtained by the sealed tube method, the oxides being heated in an excess of thioacetamide at 1200 °C.[11] In the solid phase, the "sulphiding" agent is as a rule the sulphide of the same lanthanide.[5,7,21—24] The mixture of pressed oxide and sulphide, with 20% excess of the latter, is sintered for a long time at 1300—1500 °C in a medium protecting from oxidation (*in vacuo*). The oxide sulphides obtained by this method must also be freed from the excess sulphide. The oxide sulphide having the composition $Ce_4O_4S_3$, namely $Ce_2^{3+}Ce_2^{4+}O_4S_3$, in which the cation has a mixed valence, can be obtained by the sealed tube method in which sulphur is introduced into CeO_2 by the Ce_2S_3 + S mixture at 550—600 °C.[22] Analysis of the method based on the introduction of sulphur into the oxygen compound of the lanthanide shows that the oxide sulphides formed are as a rule contaminated and that they must be subjected to additional purification in order to remove the initial compound which failed to react, or side products.

2. The Reduction of Sulphates and Sulphites

A widely used method of synthesis of the oxide sulphides involves the reduction of lanthanide sulphates, oxide sulphates, or sulphites with hydrogen,[25—33] carbon monoxide,[34—42] or natural gas[29] (Table 2). When sulphates are used, oxide sulphates are formed initially and are then reduced in accordance with the scheme

$$Ln_2O_2SO_4+4CO \rightarrow Ln_2O_2S+4CO_2.$$

If the lanthanide can exhibit an oxidation state of +2, then the sulphate is reduced consecutively: initially to $LnSO_4$, according to data for $Eu_2(SO_4)_3$,[37] then to $Ln_2O_2SO_4$, and finally to Ln_2O_2S. The reduction can be carried out either by the pure reductant or by its mixture with an inert carrier (argon, nitrogen). During the synthesis, the sulphur

Table 2. Preparation of the oxide sulphides by reducing sulphates and sulphites.

Initial compound	Reductant	Side products	t, °C	τ, h	Refs.
$Ln_2(SO_4)_3$	CO	S, CO_2	500—650	—	[34—37]
$Ln_2(SO_4)_3$	H_2	S, H_2O	800	—	[25]
$Ln_2(SO_4)_3$	H_2+N_2(1:4)	S, H_2O	800	0.5	[26]
$Ln_2(SO_4)_3$	H_2+Ar(He)	S, H_2O	500—1000	0.5—2	[27]
$Ln_2(SO_4)_3$	H_2	S, H_2O	600—700	1	[28, 29]
$Ln_2O_2SO_4$	H_2	H_2O	750	—	[25, 31]
$Ln_2O_2SO_4$	CO	CO_2	900—1050	—	[37]
$Ln_2O_2SO_4$	H_2+H_2S	H_2O	1000	2	[38]
$Ln_2O_2SO_4+(NH_4)_2CO$	H_2+Ar(He)	NH_3, H_2O	—	—	[33]
$Gd_2O_2SO_4$	H_2+Ar(96%)	H_2O	—	—	[30]
$Ln_2(SO_3)_3$[a]	H_2	S, H_2O	600—700	1	[29]
$Ln_2(SO_3)_3$	CO	LnS_x, CO_2	700—830	1	[38—40]
$Eu_2(SO_3)_3$	CO	EuS, CO_2	650	—	[41]
$Ln_2(SO_3)_3nH_2O$[b]	H_2S	LnS_x	460—630	1	[42]

[a] Natural gas (550—650 °C) was also used as the reductant. [b] Eu_2O_2S is not formed under these conditions.

oxides are reduced to elemental sulphur. An advantage of the method considered is the high rate of reaction and the relatively low temperatures of the synthesis, particularly when sulphites are used (Table 2). A single-phase product not requiring additional purification is then formed. Evidently the method can be applied in a continuous process. When the nitrogen–hydrogen mixture is used, there is no harmful waste.

3. The Oxidation of the Sulphides

The formation of oxide sulphides has been observed in the oxidation of lanthanide sulphides in air.[6,43–47] The partial oxidation of Ln_2S_3 by treatment with a mixture of water vapour and air leads to the formation of a mixture of the oxide sulphide with the sulphide and the oxide, but, at a rigorously fixed temperature, it has been possible to obtained the stoichiometric lanthanum oxide sulphide by the method of vapour phase hydrolysis.[48] The formation of oxide sulphides has been established in the oxidation under relatively mild conditions of thin films of LnS or Ln_2S_3.[46,47] The oxide sulphides are also formed *in vacuo* or in an inert medium if there is an admixture of oxygen[21,46–49] (Table 3). The formation of the oxide sulphides in the oxidation of the sulphides with sulphur(IV) dioxide[31] and carbon dioxide[4,12,50] has been noted.

Table 3. Preparation of oxide sulphides by oxidising the sulphides.

Sulphide	Oxidant and medium	Side products	t, °C	τ, h	Refs.
La_2S_3, Gd_2S_3, Y_2S_3	SO_2	—	—	—	[31]
La_2S_3	H_2O, gas	—	650–680	1	[48]
La_2S_3, LaS_2	air	SO_2	640, 620	—	[43]
La_2S_3	CO_2	S, CO	630–790	—	[12]
La_2S_3	CO_2	S, CO	1200	2	[50]
La_2S_3, Pr_2S_3, Nd_2S_3, Y_2S_3[a]	CO_2		⩾600	—	[4]
Dy_2S_3	O_2+Ar	Dy_2O_3	800–1100	—	[21]
Tm_2S_3	vacuum (10^{-3} Pa) and admixture of O_2	Tm_2O_3	430	—	[49]
EuS	air	Eu_xO_y	300–600		[6, 44, 45]
EuS	air	Eu_xO_y	660	12	[10]
CeS[b], TmS, YbS	vacuum (admixture of O_2) or air	Ln_xO_y	330	[c]	[46, 47]

[a] The sulphides of the yttrium subgroup elements are oxidised to the oxides.
[b] The intermediate $Ce_2O_2S_2$ is formed in the oxidation of CeS.
[c] Prolonged heating.

A special method of synthesis of the oxide sulphides having a non-stoichiometric composition has been proposed.[51,52] In the thermal decomposition of the thiocarbamide complexes of lanthanide acetates and propionates in an inert medium, the thiocarbamide group rearranges to the thiocyanate group and oxide sulphides having the compositions $Ln_2O_{2.6}S_{0.4}$ and $Ln_2O_{2.4}S_{0.6}$ are formed at 300–335 °C. The stoichiometric oxide sulphides are produced when homogenised mixtures of the metal carboxylate and thiocarbamide, taken in proportions of 1:3, are heated for 1 h at 300–320 °C. The product, which is contaminated with carbon, must be heated in a stream of dry CO_2 at 600–650 °C.

Thin films of the oxide sulphides, for example, Sm_2O_2S, are formed as a result of the deposition of $(CH_3)_4C_6H_{10}Sm$ + S from the gas phase at 700 °C onto a SiC support.[53] Ceramic specimens of the oxide sulphides can be obtained by heating pressed Ln_2O_2S powders at 700–1300 °C and a pressure of $(9.8–19.8) \times 10^4$ kPa for 1–5 h.[19]

Apparently lanthanum oxide sulphide was the first compound of this kind to be obtained in the single crystal state.[54] The greatest advances in this field have been achieved at the end of the 1970's and the beginning of the 1980's.[24,55–60] Different versions of the method of direct recrystallisation from solution in the melt (the Bridgman–Stockburger, Czochralski, etc. methods) are used to obtain the single crystal, the procedure involving the creation in the crucible of an inert gas counterpressure (with argon or an argon–hydrogen mixture at a pressure of 300–1500 kPa).

4. Mixed Oxide Sulphides

Oxide sulphides containing two and more lanthanides have been known for a fairly long time and are obtained by the same methods as the oxide sulphides of the individual lanthanides. However, during the last decade there has been much interest in the mixed oxide sulphides containing, apart from the traditional lanthanide, also another element, as a rule a *d* or *p* element, whose chalcogenides are used to a greater or lesser extent to prepare semiconducting materials.

The methods of synthesis of such mixed oxide sulphides are based on the familiar procedures for the preparation of "simple" compounds.[61] Mixed lanthanide oxide sulphides containing Cu(I), Ag(I), Ga, In, Ge(IV), Sn(IV), Pb(II), As(III), Sb(III), Bi(III), Cr(III), and V(III) as the second element have been synthesised hitherto.[62,63]

III. CRYSTAL-CHEMICAL PROPERTIES

1. Crystal Structure

Compounds having the general formula $(LnO)_nX$, containing the lanthanide and oxygen (Ln = lanthanide, X = oxygen, chalcogenide, halide, carbonate, orthoborate, etc. ions), have a common feature involving the presence in the structure of the $(LnO)_2^{2+}$ "complex ion", first considered by Caro.[64] This complex has a tetrahedral structure. The oxygen atom is at the centre of the tetrahedron in the sp^3-hybridised state and the corners of the tetrahedron are occupied by lanthanide ions. However, the "complex ion" cannot be identified in all the compounds containing a lanthanide and oxygen. Kuz'micheva et al.[65] specified a series of conditions for the presence or absence of such an ion in the compounds $(LnY)_2X$. The main one is the existence in the structure of different crystallographic positions for the X and Y atoms.

By combining with one another, the $(Ln_4O)_n$ tetrahedra form layers. Laruelle[66] noted that two structures of the layer are possible (Fig.1): a trigonal structure in which the triangular base of each tetrahedron is parallel to the layer, and a tetragonal structure in which the orthogonal edges of the tetrahedron are located in the planes bounding the layer. Thus the entire wide variety of the structural types of the lanthanide oxide chalcogenides is ensured by different types of alternation of the anionic lattices with layers of the $(Ln_4O)_n$ tetrahedra oriented either in accordance with the trigonal law, as happens in La_2O_2S, or in accordance with the tetragonal law, which obtains in Nd_2O_2Te. The different structures arise as a result of the formation of a superstructure, monoclinic or orthorhombic distortions, and also displacements.

A relation which makes it possible to determine the symmetry of the tetrahedral layers constituting the basis of a

particular compound has been derived[65] from the close packing principles:

$$0.78 < \frac{r + R_t}{r + R_o} < 0.96 ,$$

where r is the ionic radius of the lanthanide for a coordination number of 7 and R_t and R_o are the oxygen radii for coordination numbers 4 and 6 respectively.

If the ratio of the sums of the radii is less than 0.78, compounds of the type $(LnO)_2X$ crystallise in structural types based on the tetragonal symmetry of the layer; if it is in the range 0.78–0.96, then they are based on trigonal symmetry, and if the ratio is greater than 0.96, then the "complex ion" cannot be identified in the compound containing a lanthanide and oxygen.

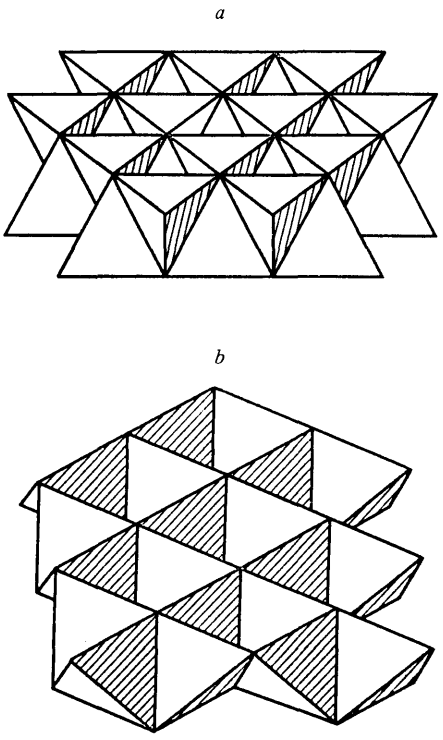


Figure 1. Trigonal (*a*) and tetragonal (*b*) construction of the $(LnO)_n^{n+}$ layer in the La_2O_2S and Nd_2O_2Te structure respectively.[62]

The structure of the lanthanide oxide sulphides having the composition Ln_2O_2S is based on a tetrahedral layer with trigonal symmetry and they are all isostructural for the entire series of lanthanide metals.[17] The structure of La_2O_2S can be derived from that of Ce_2O_3 by replacing an oxygen atom in the octahedral environment by a sulphur atom.[67] Fig. 2 presents projections of the La_2O_2S structure onto the xy and yz basal plane and also the coordination polyhedra around the La atoms.

Investigators have frequently attempted to refine the structure of Ln_2O_2S. One of such refinements has been carried out by means of the X-ray diffraction analysis of La_2O_2S : Nd single crystals, obtained by Czochralski's method,[55] on an autodiffractometer.[64] Polycrystalline Ho_2O_2S [69] and Nd_2O_2S [70] have been investigated by neutron diffraction at 300 and 4 K respectively. The thermal and positional parameters were refined as in the previous study. The large error in the determination of the thermal isotropic factors or even their negative values in the case of Nd_2O_2S can be explained by the presence in the specimen of a second phase, namely $Nd_2O_2S_2$:[70] no explanation has been found for Ho_2O_2S.[69] An attempt has been made to refine the multiplicity of the positions of sulphur in Ho_2O_2S.[70] The desirability to refine the populations of the different positions by sulphur atoms was justified by the possibility of the partial substitution of sulphur by oxygen. It was found that the population exceeds the multiplicity [number?] of the positions occupied, which can be in no way accounted for by the substitution of sulphur by oxygen. Nevertheless the refinement of the sulphur content made it possible to reduce somewhat the R factor.

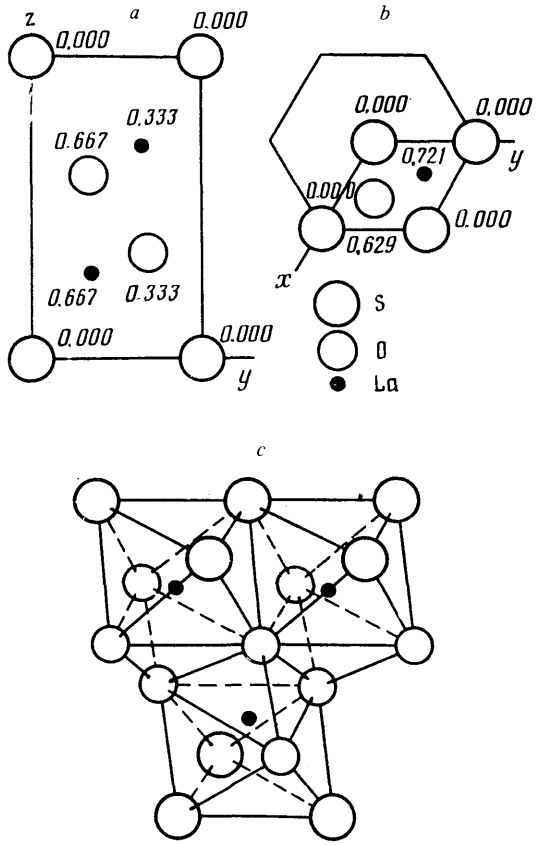


Figure 2. Projection of the La_2O_2S structure onto the yz (*a*) and xy (*b*) planes and the interlinking of the polyhedra around the La atoms (*c*). The numbers indicate the height along the $x(z)$ axis.

The structures of La_2O_2S : Ln single crystals, obtained by the modified Stockburger–Bridgman method,[57] have been investigated[71,72] on an autodiffractometer. According to the X-ray diffraction data, the crystals have a deficiency of sulphur and the metal, while the population of the oxygen sites is excessive.[71] Allowance for the partial incorporation

of sulphur in the oxygen sublattice and for the incorporation of oxygen in the sulphur sublattice (on the assumption that the sites are filled to the maximum extent) made it possible to reduce the *R* factor and to obtain crystal-chemically acceptable formulae of the compounds.[72] In the calculation of the difference electron density, a maximum was observed for the 0 0 1/2 site. This region of "concentrated" electron density was interpreted as interstitial atoms of neutral sulphur, occupying approximately 5% of these positions. However, one cannot rule out the possibility that lanthanum ions (or the ions of another lanthanide) are located at a low concentration in these positions.† These results were confirmed by the study of La_2O_2S : Ln single crystals by the chemical and neutron activation methods and by hydrostatic weighing.[72]

Thus crystal-chemical formula of lanthanum oxide sulphide can be written in the general form

$$La_{2-x}[\ ]_xO_{2-y}[\ ]_yS_{1-z}[\ ]_z\,(S_w^0)$$

where [ ] denotes vacancies here and henceforth. The formation of the principal point defects in La_2O_2S can be described by the following equation (in terms of the Kröger–Wink notation[73]):

(a) Schottky disordering reaction;

$$0 \rightleftarrows 2V_{La}^{\cdot\cdot\cdot} + 2V_O^{\cdot\cdot} + V_S^{\cdot\cdot}.$$

(b) Frenkel' disordering reaction:

$$La_{La}^{x} + V_i^{x} \rightleftarrows La_i^{\cdot\cdot\cdot} + V_{La}^{\prime\prime\prime},$$

$$S_S^{x} + V_i^{x} \rightleftarrows S_i^{x} + V_S^{x}.$$

(c) Interfacial reactions at the crystal–vapour interface:

$$S_S^{x} \rightleftarrows 0.5S_2(gas) + V_S^{\cdot\cdot} + 2e^{\prime},$$

$$O_O^{x} \rightleftarrows 0.5O_2(gas) + V_O^{\cdot\cdot} + 2e^{\prime}.$$

(d) Antistructural defects or atoms at "foreign" sites:

$$S^{x} + V_O^{x} \rightleftarrows S_O^{x},$$

$$O^{x} + V_S^{x} \rightleftarrows O_S^{x}.$$

In the equations the dots, primes, and crosses denote positive and negative charges and neutral atoms respectively.

In principle there is a possibility of the formation of partly ionised or neutral defects[74] (for example, apart from the $V_S^{\cdot\cdot}$, $V_O^{\cdot\cdot}$, and $V_{La}^{\prime\prime\prime}$ forms, the vacancies can exist as $V_{La}^{\times}$, $V_{La}^{\prime\prime}$, $V_{La}^{\prime}$, $V_S^{\times}$, $V_S^{\cdot}$, $V_O^{\times}$, and $V_O^{\cdot}$). In this case the equations for defect formation presented here are supplemented by others. It has been shown[75,76] that, under the influence of pressure, the lanthanum oxide sulphide specimens change colour: at a low pressure, the colour of the specimens becomes pink, i.e. a colour centre, the so called *F*-centre $(V_S^{\cdot}, e^{\prime})^{\times}$, is formed.

The results obtained for the defect formation have served as the basis of the mechanisms of diffusion in lanthanum oxide sulphide# and also of a high-speed method for the determination of the composition and the extent of defect formation according to X-ray diffraction data.§

2. The Region of Homogeneity

The La–O–S ternary system has not so far been fully investigated. The phase regions and the phase crystallisation conditions are unknown. Only the liquidus line for the compositions of the La_2S_3–La_2O_3 quasi-binary section (Fig.3),[77] having two maxima, has been determined. One of the maxima corresponds to La_2O_2S with a melting point of 2080°, which agrees well with the value found previously (2070 °C).[54] The second maximum corresponds to the composition La_2OS_2, which melts at 1960 °C.

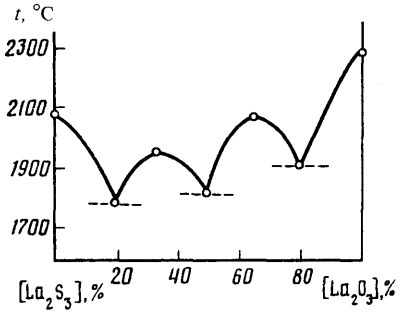


Figure 3. The liquidus in the La_2S_3–La_2O_3 system.[77]

In a study of the La_2S_3–La_2O_3 system,[78] the specimens were obtained by the method inovlving the solid-phase sintering of lanthanum sesquioxide and sesquisulphide *in vacuo* or in an atmosphere of argon (pressure 1–2 atm) at 1100–1200 °C for 4 h. A broad region corresponding to the existence of the lanthanum oxide sulphide phase having the composition

$$La_{2\pm x}O_{2\pm y}S_{1\pm z}$$

was established from the X-ray diffraction data. In the region of homogeneity, the plots of the variation of the lattice periods (Figs.4*a* and 4*b*) have a point of inflection corresponding to the composition La_2O_2S. The decrease in the periods on passing from La_2O_2S to La_2O_3 can be associated both with the subtraction of sulphur and metal via the

$$La_{2-x-2/3}[\ ]_{2x}O_2S_{1-x}[\ ]_x,$$

mechanism and with the substitution of sulphur by oxygen: $La_2O_2(S_{1-x}O_x)$. In the composition range La_2O_2S–La_2S_3, the decrease in the lattice period can be explained by the subtraction of oxygen and the metal, i.e.

$$La_{2-x-2/3}[\ ]_{x-2/3}O_{3-x}[\ ]_xS,$$

and also by the substitution of oxygen by sulphur, i.e. $La_2(O_{2-x}S_x)S$. The type of the solid solutions was established by measuring the density of the test specimens. Its variation within the limits of the region of homogeneity corresponds exactly to the substitution mechanism (Fig.4*c*). The composition $La_2O_{2.14}O_{0.86}$ corresponds to the boundary of the region of homogeneity on the La_2O_3 side, while the composition $La_2O_{1.71}S_{1.29}$ (1100 °C, 0.1 Pa) corresponds to the boundary on the La_2S_3 side (Fig.4*a*). At 1200 °C, the boundary specimens have the compositions $La_2O_{1.81}S_{1.18}$ and $La_2O_{2.09}S_{0.91}$ (Fig.4*b*), but one can hardly speak of a narrowing of the region of homogeneity with increase in temperature, because the results obtained vary within the limits of the accuracy of the phase analysis. Furthermore, there are

†See G.M.Kuz'micheva, I.V.Perepelkin, N.V.Porotnikov, and D.S.Kholodnyi, Zhur.Neorg.Khim., 1985, **30**, 2981 [Russ.J.Inorg.Chem., 1985(11)].

#See G.P.Borodulenko, A.A.Eliseev, G.M.Kuz'micheva, et al., Zhur.Neorg.Khim., 1986, **31**, 567 [Russ.J.Inorg. Chem., 1986(3)].

§See G.M.Kuz'micheva, I.V.Perepelkin, and A.A.Eliseev, Zhur.Neorg.Khim., 1986, **31**, 2527 [Russ.J.Inorg.Chem., 1986(10)].

no grounds for the assumption that the defect-free crystal lattice with fully occupied atomic sites corresponds to the composition La_2O_2S.

Analysis of studies on the Ln–S–O systems, where Ln ≠ La, can also be of definite interest.[21,104] One of these has been devoted to the investigation of the Dy–S–O system in the region of homogeneity of dysprosium oxide sulphide.[21] Homogeneous specimens of dysprosium oxide sulphide having the general formula $Dy_2O_{2+x}S_{1+x}$ were synthesised by heating in a vacuum furnace (p < 0.1 Pa) mixtures of Dy_2O_3 and Dy_2S_3 at 1300 °C for 5 h and at 1600 °C for 3 h. The region of homogeneity in the temperature range 1300–1600 °C (for quenched specimens) hardly varies and extends from 19 (in the case of $Dy_2O_{2.05}S_{0.95}$) to 23 at.% of sulphur ($Dy_2O_{1.85}S_{1.15}$). The variation of only the period c was observed in this composition range, while the period a remains constant within the limits of the error of the determination (±0.003 Å). This character of the variation of the lattice parameter of Dy_2O_2S with the sulphur content indicates the formation of substitutional solid solutions in the concentration range indicated.

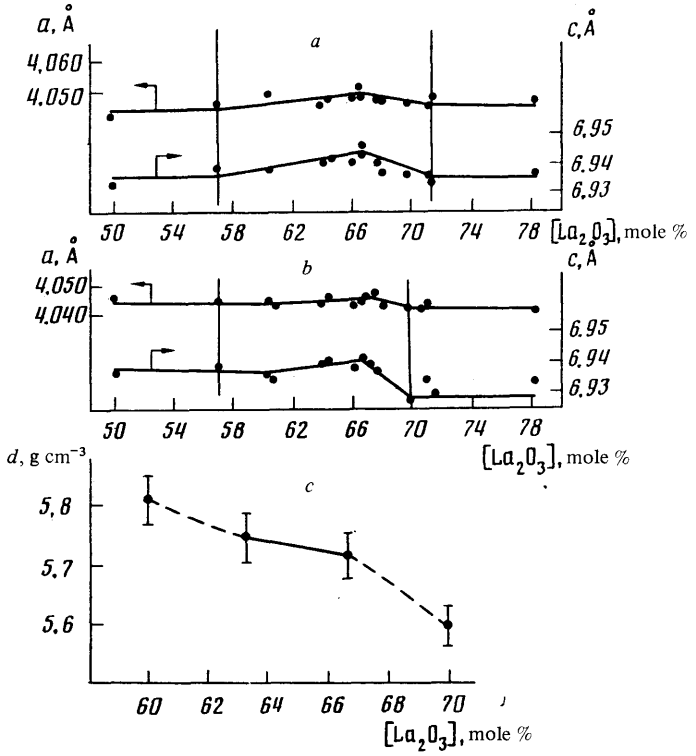


Figure 4. Variation of the lattice periods (a, b) and of the densities (c) of lanthanum oxide sulphide at 1100 °C (a) and 1200 °C (b and c) *in vacuo* along the La_2S_3–La_2O_3 section.[78]

IV. SOLID SOLUTIONS IN THE Ln'_2O_2S–Ln''_2O_2S SYSTEM

A number of studies[8,29,40,79–81] have been devoted to solid solutions of the type $(Ln', Ln'')_2O_2S$. In particular the La_2O_2S–Ln_2O_2S systems, where Ln = Nd, Sm, Eu, Gd, Dy, Yb, Lu, or Y, have been examined.[40] Total miscibility has been observed only in the La_2O_2S–Nd_2O_2S and La_2O_2S–Sm_2O_2S systems, while in the remaining systems there are two-phase regions. The possibility of the existence of solid solutions is determined by the ratio of the ionic radii: a continuous series of solid solutions are formed for

$$[R(La^{3+}) - R(Ln^{3+})]/R(Ln^{+3}) < 9\%$$

Apart from the $(La, Ln)_2O_2S$ systems, Leskela[38] also investigated systems based on yttrium oxide sulphide: Y_2O_2S–Nd_2O_2S and Y_2O_2S–Eu_2O_2S (Fig.5). The above dimensional criterion is valid also in this case: in the former system ($\Delta R/R$ = 9.2%), a limited miscibility is observed, while in the latter ($\Delta R/R$ = 5.2%) the miscibility is complete. The specimens for the investigations were prepared by the reduction of coprecipitated lanthanide sulphates with carbon monoxide at 800 °C.

It has been stated[40] that the limit of the two-phase regions as well as the lattice period depend on the method of preparation of the $(Ln', Ln'')_2O_2S$ powders. Indeed the miscibility in the La_2O_2S–Y_2O_2S specimens obtained by "sulphiding" in a stream of $0.2H_2S + 0.8N_2$ (1200–1250 °C) a homogeneous mixture of coprecipitated lanthanide oxide powders[79] is somewhat different from that in the analogous system described by Leskela and Ninisto.[40] This difference cannot be explained by the different temperature of the synthesis, because the two-phase region does not become narrower on raising the temperature from 800 °C [40] to 1200 °C [79] and its width remains unchanged, the region being merely displaced towards La_2O_2S. On the other hand, the lattice periods of individual oxide sulphides in the La_2O_2S–Gd_2O_2S system, found in the above two investigations,[40,79] are identical, although a different value has been obtained for the La_2O_2S–Y_2O_2S system.

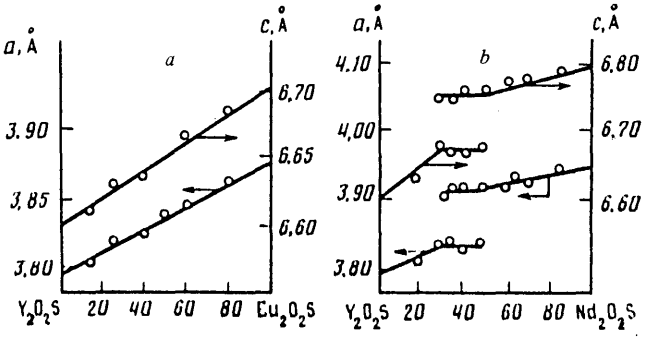


Figure 5. Variation of the lattice periods as a function of the composition of the Y_2O_2S–Eu_2O_2S (a) and Y_2O_2S–Nd_2O_2S (b) systems.[40]

Completely different results for the miscibility of the oxide sulphides have been published in a study[88] where the existence of a continuous series of solid solutions in the La_2O_2S–Ln_2O_2S systems (Ln = Pr, Eu, or Yb) was discovered. The $(La, Pr)_2O_2S$ solid solutions were obtained by oxidising a mixture of the polysulphides in a stream of $H_2 + H_2O$ (3 vol.% H_2O) for 3–4 h at 520 °C. The $(La, Eu)_2O_2S$ and $(La, Yb)_2O_2S$ specimens were obtained by introducing sulphur in the liquid phase into the corresponding solid solutions of the oxide carbonates (500–700 °C, 4–5 h). The lattice periods of the individual oxide sulphides in these systems, quoted in the above investigations,[40,79] are the same within the limits of experimental error and the temperatures of the synthesis are similar.

An attempt has been made[82] to calculate the binodal curve for the decomposition of the solid solutions in the La_2O_2S–

Ln_2O_2S systems by the method of Urusov and co-workers[83,84] in order to elucidate the influence of various factors on the width of the region of homogeneity. The calculation is based on the principle that the Gibbs free energy of mixing tends to a minimum, which also determines the state of equilibrium in the isomorphous mixture; the vibrational and configurational entropies were taken into account. This calculation made it possible to explain the discrepancies between the limits of miscibility in the La_2O_2S–Ln_2O_2S systems and to demonstrate the marked dependence of the limits of the region of homogeneity on the method of preparation of the solid solutions, which determines the common structural unit and the degree of defectiveness of the initial components.

V. THERMAL AND THERMODYNAMIC PROPERTIES

The oxide sulphides Ln_2O_2S occupy an intermediate position, as regards composition, in the Ln_2S_3–Ln_2O_2S–Ln_2O_3 series. They differ from the sulphides by a greater thermal stability in an oxidising medium but are greatly inferior to the oxides in this respect. The thermal stability of the oxide sulphides in an inert medium (argon) has been determined for both the individual and the erbium-, ytterbium-, and neodymium-activated lanthanum oxide sulphide.[85,86] Lanthanum oxide sulphide is stable up to 1450 °C, but, starting from 1500 °C, when the specimens have been maintained for 1 h under the given conditions, the stoichiometry of the oxide sulphide phase changes. At higher temperatures the oxide sulphide evaporates and dissociates; the composition of the gas phase is complex and has not been established unambiguously. Fused lanthanum oxide sulphide is gradually depleted in sulphur and its loss reaches 30% after the melt has been allowed to stand for 5 h.[55]

The thermal properties of the oxide sulphides on heating in an oxidising medium (air) have been studied by many investigators.[30,81,87–93] It has been established by various methods of thermal analysis (thermogravimetric, derivatographic measurements, and differential thermal analysis) that the oxide sulphides are oxidised by air directly to the oxide sulphates $Ln_2O_2SO_4$. However, it has been observed by the derivatographic method that praseodymium, europium, and gadolinium oxide sulphides are oxidised in air in two stages.[90,92,93] The oxidation of Gd_2O_2S in the first stage is accompanied by the formation of an intermediate oxide sulphite phase having the composition $Gd_2O_2SO_3$. Presumably, the oxide sulphite is formed initially as an intermediate in the oxidation of praseodymium and europium oxide sulphides. The oxide sulphites of the above metals are stable within a narrow temperature range and are oxidised to the oxide sulphates at a higher rate than the oxide sulphides.[92] The fact that the formation of the oxide sulphites has not been observed in all the cases investigated confirms their thermal instability. In pure oxygen, the oxidation of oxide sulphides is rapid. The temperatures of the onset of the activation of Ln_2O_2S and the temperature ranges where these compounds are oxidised to the oxide sulphates differ by 80–100 °K in the above studies, which can be explained by the different purities of the specimens, the different conditions in their preparation (disc or powder), and the different methods of investigation, i.e. the specific features of the study of the heterogeneous system under non-equilibrium conditions.

The temperature ranges of the stability and of the onset of oxidation of lanthanide oxide sulphides are arranged systematically in Table 4. Overall, the polycrystalline lanthanide oxide sulphides are stable in air up to 450–500 °C, but Ce_2O_2S begins to oxidise already at temperatures above 180 °C.[7] The rate of oxidation at the beginning of the process is low, but, above a certain temperature limit which depends on the type of the lanthanide, it increases sharply. The temperature of the onset of oxidation increases in the sequence La_2O_2S–Lu_2O_2S, Y_2O_2S, occupying an intermediate position in the middle of the series. The oxide sulphates, the final sulphur-containing products of the oxidation of the oxide sulphides, are more stable; their stability decreases in the sequence La–Lu, Y occupying the position after Dy. When the rate of heating is reduced from 10 to 1 K min^{-1}, the temperatures of the onset of the oxidation of La_2O_2S and Y_2O_2S decrease from 765–770° to 620–640 °C. The stability of the oxide sulphides is influenced by the degree of crystallinity of the specimens. After they have been kept in an inert medium (nitrogen), the temperature of the onset of oxidation increases by ~100 K and the rate of oxidation falls.

Table 4. The oxidation temperatures of the lanthanide oxide sulphides.

Oxide sulphide	t_o, °C	$t_{0.5}$, °C (Refs.88, 89)	Oxide sulphide	t_o, °C	$t_{0.5}$, °C (Refs.88, 89)
La	500–800 [90]	765	Gd	700–1000 [30]	—
La	510–910 [32]	—	Gd	450–630 [90]	—
La	650–680 [86]	—	Tb	620–690 [90]	710
La	960[a] [60]	—	Dy	—	740
Ce	>180 [7]; 300–600 [91]	—	Ho	—	800
Pr	530–650 [90]	715	Er	—	835
Nd	610–680 [90]	720	Tm	—	840
Sm	630–930 [11]	800	Yb	—	790
Sm	650–780 [90]	—	Lu	635–850 [32]	770
Eu	300–680 [45]	750	Y	595–950 [32]	790
Eu	380–580 [81]	—	Y	750–950 [18]	—
Eu	500–570 [90]	—	Y	990[a] [60]	—
Gd	470–855 [32]	800			

Notation. t_o is the temperature of the onset of oxidation or the range of oxidation temperatures, $t_{0.5}$ is the temperature corresponding to the oxidation of 50% of the oxide sulphide.

[a] Single crystal.

Note. The numbers in square brackets denote references (Ed. of Translation).

Table 5. The oxidation temperatures of the solid solutions $(La, Y)_2O_2S$ and $(Eu, Y)_2O_2S$.[81]

Composition[a]	t_o, °C	t_d, °C	Composition[b]	t_o, °C	t_d, °C
Eu_2O_2S	510	1280	La_2O_2S	640	1470
$(Eu_{0.8}Y_{0.2})_2O_2S$	535	1270	$(La_{0.8}Y_{0.2})_2O_2S$	705	1445
$(Eu_{0.6}Y_{0.4})_2O_2S$	550	1255	$(La_{0.6}Y_{0.4})_2O_2S$	740 and 790[c]	1250; 1430
$(Eu_{0.4}Y_{0.6})_2O_2S$	560	1200	$(La_{0.4}Y_{0.6})_2O_2S$	660 and 720[c]	1220; 1350
$(Eu_{0.25}Y_{0.75})_2O_2S$	585	1185	$(La_{0.2}Y_{0.8})_2O_2S$	780	1190
Y_2O_2S	720	1170	Y_2O_2S	720	1170

Notation: t_o is the temperature of the onset of oxidation and t_d the decomposition temperature of the oxide sulphate.

[a] The composition of a continuous solid solution is quoted.
[b] The composition of a solid solution with limited miscibility is quoted.
[c] Two-stage oxidation.

The thermal oxidation of solid oxide sulphide solutions depends on the type of the solid solution (Table 5). The continuous solid solutions (Eu_2O_2S–Y_2O_2S) are oxidised as individual compounds. The temperature of the onset of

oxidation then diminishes with increase in the content of the less stable component and the temperature limits of the stability of the oxidised phase increase, i.e. a dependence of the thermal stability on the mole fractions of the components of the pseudobinary system is observed. The solid solutions with limited miscibility (when the difference between the ionic radii of the lanthanide is greater than 10%) are oxidised to the oxide sulphates in two stages and the oxide sulphate phases also decompose into two stages.

In view of the instability of the oxide sulphides in oxidising and inert media at elevated temperatures, the determination of their melting points involves considerable experimental difficulties. The melting points of many oxide sulphides are therefore either unknown or have been determined with inadequate accuracy. The melting points indicated in the literature (Table 6) indicate, with the apparent exception of the melting point of La_2O_2S, the temperature range of the fusion of oxide sulphates rather than characterising the individual compounds.

Table 6. The melting points of the oxide sulphides.

Ln	M.p., °C	Refs.	Ln	M.p., °C	Refs.
Y	2120	[95]	Nd	1990	[96]
La	2070±30	[54]	Sm	1980	[96]
La	2080	[77]	Gd	>2000	[54]
La	1940	[96]			
Ce	2000±200	[3]			
Ce	1950	[95]			

The phase equilibria in the oxide sulphide systems have been studied only for the La–S–O system.[77,94] The equilibrium compositions of the La_2O_3(B), LaS_2, La_2S_3, $La_2O_2SO_4$, La_2O_2S, and $La_2O_2S_2$ phases coexisting at 800 °C have been established[94] (Fig.6). These data confirm the formation of La_2O_2S, detected previously in a study of the T–x section of the diagram for the La_2S_3–La_2O_3 system.[77] The above studies[77,94] are at present the only fundamental investigations which have been made on the phase equilibria in the oxide sulphide systems.

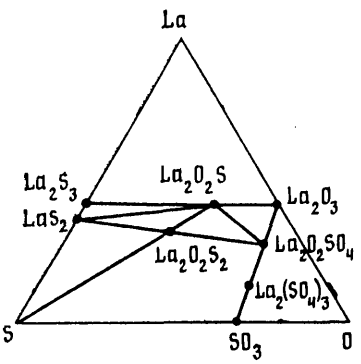


Figure 6. Isothermal section through the phase diagram for the La–S–O system (at 1073 K).[94]

The knowledge of the thermodynamic properties makes it possible to determine the conditions under which perfect oxide sulphide single crystals can be grown, for example, from their melts. Since the melts dissociate with evolution of gases which also contain elemental sulphur, the thermodynamic parameters are essential for calculations of the equilibrium pressure of the gas phase over the melt.

In an experimental study of the thermochemical properties of the oxide sulphides, it has been established that,[93,97–99] in a sulphuric acid solution of cerium(IV) sulphate, the oxidation proceeds in accordance with the equation

$$Ln_2O_2S(cryst.) + Ce(SO_4)_2(soln) + H_2SO_4(soln) \rightarrow$$
$$Ln_2(SO_4)_3(soln) + Ce_2(SO_4)_3(soln) + S_{orthorhomb} + H_2O(soln).$$

The enthalpies of these reactions have been measured by calorimetric methods and the standard enthalpies of formation of lanthanum, praseodymium, neodymium, and samarium oxide sulphates have been determined. The enthalpies of formation of europium and gadolinium oxide sulphates listed in Table 7 were calculated from the enthalpies of solution of the compounds in aqueous hydrochloric acid saturated with hydrogen sulphide (Table 7). The calculated enthalpies of formation of the oxide sulphides[100,101] differ from the experimental values by 85–100 kJ mol^{-1}. Consequently the theoretically deduced probable dissociation reactions of La_2O_2S [102] and the excess pressure of the gas phase over the melt necessary in order to be able to grow single crystals must be regarded as approximate.

Table 7. Thermodynamic functions of the oxide sulphides calculated from literature data.[93,97–99,104–110,114,116,117]

Compound	$-\Delta_fH^0$(298.15 K), kJ mol^{-1}	S^0(298.15 K)[a], J mol^{-1} K^{-1}	Δ_fG^0[b], kJ mol^{-1} (T, K)
La_2O_2S	1660.5±7.6	33.8	1538.7 (298 K)
	—	32.9	—
	—	34.8	—
Ce_2O_2S	1423.0±12	33.8	1423±12.6 (1072 K)
	1770.7±63 (1410 K)	34.4	1301.5 (1410 K)
Pr_2O_2S	1639.7±21	41.1	1425.1±62.8 (1072 K)
	—	34.2	1414.2±18.8 (1072 K)
	—	—	1514.9 (298 K)
Nd_2O_2S	1646.9±21	40.6	1523.3 (298 K)
	—	34.1	
Sm_2O_2S	1642.6±9.5	39.0	1517.9 (298 K)
	—	34.0	—
Eu_2O_2S	1469.0±8.9	38.4	1338.9 (298 K)
Gd_2O_2S	1644.9±4.0	38.4	1520.2 (298 K)
Y_2O_2S	—	30.2; 27.1; 28.8	1482.4±12.6 (1068 K); 1493.7±84 (1068 K)
Sc_2O_2S	—	21.3	—

[a] Approximate entropies obtained by different workers.
[b] The adjustment of the values of Δ_fH^0(298.15 K) and $\Delta_fG^0(T, K)$ for self-consistency is impossible owing to the lack of the temperature variation of the heat capacities of Ln_2O_2S and $Ln_2O_2SO_4$; the calculation of Δ_fH^0(298.15 K) from the temperature variation of $\Delta_fG^0(T, K)$ is also impossible for the same reason.

A tensimetric study of the CeO_x–CO–SO_2 equilibrium[103] and of the Eu_2O_3–H_2S–H_2–CO system[10] made it possible to calculate for the reactions

$$2CeO_2(cryst.) + 4CO(gas) + SO_2(gas) \rightarrow Ce_2O_2S(cryst.) + 4CO_2(gas)$$
(900–1400 °C)
$$4EuS(cryst.) + 2O_2(gas) \rightarrow 2Eu_2O_2S(cryst.) + S_2(gas)\ (900°).$$

the equilibrium pressures of the gaseous components and the Gibbs free energies of formation of cerium and europium oxide sulphides, which are also listed in Table 7.

The oxidation of the oxide sulphides in accordance with the equations

$$Ln_2O_2S(cryst.) + 2O_2(gas) \rightarrow Ln_2O_2SO_4(cryst.),\ Ln = Ce, Y;$$

$$Ln_2O_2S(cryst.) + 0.5O_2(gas) + 2Ag(cryst.) \rightarrow Ln_2O_3(cryst.) + Ag_2S(cryst.),$$
$$Ln = La, Nd\text{-}Dy,$$

has been studied thermodynamically by an e.m.f. method using an oxygen ion solid electrolyte based on zirconium oxide.[105-110] The temperature dependence of the Gibbs free energy of the first of the above reactions has been found. The thermodynamic properties of the oxide sulphides (Table 7) and their enthalpies of oxidation (Table 8) were calculated by the present authors from the relations obtained. The values found made it possible to plot thermodynamic diagrams for the coexistence of the oxide, sulphide, and oxide sulphide phases[111-115] as a function of the partial pressures of O_2 and S_2 (Fig.7).

Table 8. The enthalpies of the oxidation of the oxide sulphides via the reactions $0.5\ Ln_2O_2S(cryst.) + O_2(gas) \rightarrow 0.5Ln_2O_2SO_4(cryst.)$.

Ln	ΔT, K	T_{av}, K	$\Delta H^0(T_{av}, K)$	$\Delta G^0(T_{av}, K)$
La	940—1250	1095	457±1.5	287±57
La	1100—1500	—	459.84	—
La	1190—1510	1350	—	477.7±3.8
Pr	1100—1400	1250	447.12	—
Nd	930—1200	1065	—	480.4±0.6[b]
Nd	1170—1400	1455	—	755±5
Sm	1050—1370	1160	453.44	—
Eu	1020—1320	1170	447.0	—
Gd	1000—1280	1140	445.57	908.5±6.5[c]
Tb	1020—1200	1110	453.48	—
Dy	1040—1180	1110	445.74	—
Ho	1000—1400	1250	446.9[a]	—
Er	1000—1400	1250	446.2[a]	—
Tm	1000—1400	1250	445.4[a]	—
Yb	1000—1400	1250	444.6[a]	—
Lu	1000—1400	1250	443.9[a]	—
Y	1190—1500	1345	—	1108.9±5.8

[a] Estimated quantities.
[b] At 1285 K.
[c] At 1380 K.

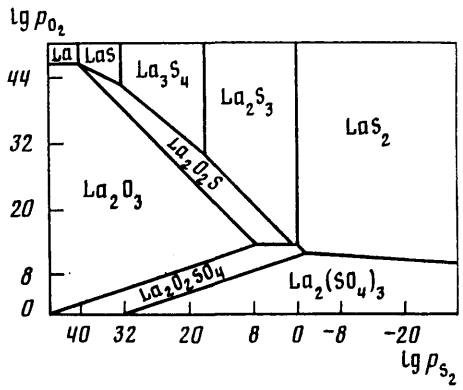


Figure 7. Isothermal section through the phase diagram for the La–S–O system (at 1100 K).

The standard entropies of the oxide sulphides have been estimated in a number of studies.[93,97,116,117] The values obtained have been used to calculate standard thermodynamic functions (Table 7) and, in particular, the Gibbs free energies, from which the equilibrium constants and the equilibrium vapour pressures of sulphur necessary for the selection of optimum conditions for the growing of perfect single crystals were calculated.

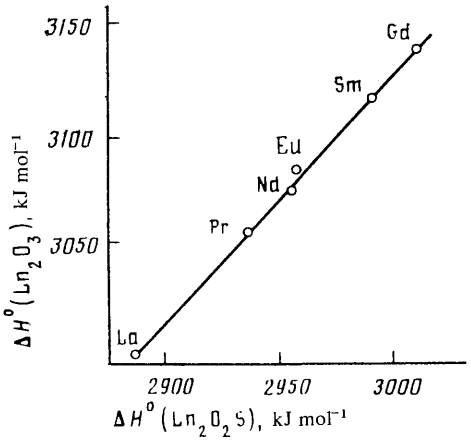


Figure 8. Relation between the crystal lattice energies of the lanthanide oxides and oxide sulphides.

Comparison of the thermodynamic functions of the oxide sulphides, sulphides, and oxides shows that the energies of formation of the compounds increase in the sequence Ln_2S_3–Ln_2O_2S–Ln_2O_3. This sequence agrees in principle with the increase in thermal stability and melting points. The rule of additivity does not then hold when sulphur is replaced by oxygen. Thus the complete oxidation of the sulphide to the oxide ($La_2S_3 + 4.5O_2 \rightarrow La_2O_3 + 3SO_2$) results in the evolution of 120 kJ per mole of S, while the oxidation of the oxide sulphide to the oxide ($La_2O_2S + O_2 \rightarrow La_2O_3 + SO_2$) is accompanied by the evolution of 100 kJ per mole of S. Analogous thermodynamic properties in the series of lanthanide oxides and oxide sulphides vary in parallel, which is illustrated, in particular, in Fig.8.

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As can be seen from the data presented, the methods of synthesis and the crystal chemistry of the oxide sulphides have been investigated fairly completely. The thermodynamics of the lanthanide, scandium, and yttrium oxide sulphides have been investigated to a lesser extent. There are no consistent values of the principal thermodynamic functions and no reliable melting points, which could be used to characterise newly obtained compounds. Bearing in mind the applied importance of the oxide sulphides, namely their generally established application in the technology of phosphors, as well as the possible new fields where they may be used in the desulphurisation of metallic melts and steels and in the removal of sulphur and its gaseous compounds (H_2S, SO_2) from furnace gases and gaseous fuel, the necessity for further investigation of the high-temperature chemistry and thermodynamics of the oxide sulphides becomes understandable.

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Oxidative Condensation of Methane—a New Pathway to the Synthesis of Ethane, Ethylene, and Other Hydrocarbons

Kh.M.Minachev, N.Ya.Usachev, V.N.Udut, and Yu.S.Khodakov

During the last five years, the chemistry of methane has been enriched by the possibility of obtaining C_2 and other hydrocarbons as a result of the oxidative condensation of methane in the presence of a series of catalytic systems. The availability of the starting materials (CH_4 and O_2) leads to extensive prospects for the replacement of the petroleum raw materials by natural gas in single-stage syntheses of valuable compounds and in the first place ethylene. This review gives a systematic account of the results of the selection of effective catalysts and surveys the information leading to the elucidation of the mechanism for the formation of the products of the extensive oxidation and oxidative condensation of methane. The bibliography includes 118 references.

CONTENTS

I. Introduction 221
II. Catalysts of the oxidative condensation of methane 221
III. The mechanism of the oxidation reactions of methane 227

I. INTRODUCTION

Methane has long attracted the attention of chemists as the starting material for the synthesis of valuable products,[1] but its high stability hinders its processing.[2] At the present time the bulk (more than 90%) of the natural gas extracted is used as fuel, although there exist industrial methods for the conversion of methane into a synthesis gas, chloro-derivatives, and acetylene.[3] The activation of CH_4 molecules, for example, for the manufacture of acetylene, is achieved at high temperatures (about 1500 °C),[1] which is due to the thermodynamic factors governing this process.

In connection with the problem of involving methane in chemical reactions studies[4-6] on its activation under comparatively mild conditions by transition metal complexes are of considerable interest. Thus at 90–120 °C and a methane pressure of 100 atm, methane is oxidised in an aqueous solution of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ to CH_3OH and CH_3Cl with stoichiometric reduction of platinum(IV) to platinum(II).[4] Studies[6] on the oxidation reactions of methane under the influence of oxygen, especially its oxidation to methanol and formaldehyde, have a clear-cut practical purpose.[6] In the presence of one of the most active molybdenum-containing catalysts at 450 to 500 °C and a pressure of 50 atm, the yields of CH_3OH and CH_2O relative to the methane which has reacted reach 50–75% and 4–8% respectively for an overall conversion of methane up to 3.5%. Methods for the gas-phase oxidation of methane by atmospheric oxygen with added initiators (nitrogen oxides) are also known,[6] but the low yield of the target products hinders their practical application. In order to increase the selectivity of the formation of methanol and formaldehyde, it has been suggested[6] that N_2O be used as the oxidant, which makes it possible to avoid the extensive oxidation of methane, although the degree of conversion of the latter does not then increase and amounts to ~2%.

In the oxidation of methane with N_2O in the presence of high-silica zeolites, the formation of aliphatic and aromatic hydrocarbons is observed at a reaction temperature of 300 to 600 °C.[7-12] The dependence of the yield of hydrocarbons of different classes on temperature and on the degree of elimination of metal cations from zeolites shows that methanol, the primary methane oxidation product,[8] undergoes reactions characteristic of catalysis by high-silica zeolite (HSZ).[7] It is noteworthy that the replacement of N_2O by oxygen under the same conditions leads to the formation of the products of the extensive oxidation of methane.[8] Studies[13-15] on the oxidative coupling of methane to substances whose molecules contain methyl groups (toluene, acetonitrile) are of interest; this results in the formation of vinyl derivatives (styrene, acrylonitrile). As in the previous case, oxygen-containing methane oxidation products (CH_3OH, CH_2O) probably enter into the coupling reaction, but their yield is unfortunately low.

A new aspect of the methane chemistry arose as a result of studies by Mitchell[16-18] and Keller and Bhasin[19] in which C_2 and other hydrocarbons were detected after methane had been allowed to come into contact with the oxides of a number of metals at temperatures above 600 °C. The formation of, for example, ethane under these conditions takes place via the oxidative condensation of methane:

$$2CH_4+[O]\rightarrow C_2H_6+H_2O\,.$$

The participation of oxygen (in the given instance of the oxygen from the oxide, which plays the role of a solid oxidant) is an essential condition for the elimination of thermodynamic limitations to the formation of the C–C bond from the CH_4 molecules.[19]

The results of the above studies[16-19] stimulated research into the oxidative condensation of methane, which has led to the discovery of a direct pathway to the preparation from natural gas of a number of hydrocarbons and especially ethylene, whose synthesis had been based hitherto on the processing of petroleum raw material. The present review surveys and gives a systematic account of the results obtained in the selection of catalytic systems for the oxidative condensation of methane and analyses data concerning the conditions and mechanisms of the reactions leading to the formation of C_2 and other hydrocarbons from methane.

II. CATALYSTS OF THE OXIDATIVE CONDENSATION OF METHANE

The deliberate search for effective catalysts of the effective condensation of methane, which has been prosecuted simultaneously by many research groups in the USSR, Japan, the USA, and the Federal Republic of Germany, established the principal features of the catalytic reactions of methane in the presence of systems of different chemical composition. Among the catalysts investigated, three main classes, embracing oxide systems, oxide systems with alkaline additives, and catalysts containing halogen compounds, may be

distinguished. This classification reflects not only the greater complexity of the catalytic systems but also takes into account their greater effectiveness in the formation of C_2 and other hydrocarbons in the oxidation reactions of methane.

1. Oxide Systems

The results of a systematic study[19] of the oxidative condensation of methane in the presence of various oxides deposited on α-Al_2O_3 in amounts of 5–10 wt.% were published in 1982. The reaction was carried out in the presence of catalysts subjected to preliminary treatment with oxygen. The highest activity in the formation of C_2 hydrocarbons (ethane and ethylene) was shown by manganese, thallium, cadmium, and lead oxides (Table 1). Catalysts containing Zn, Ti, Zr, Mo, Fe, Cr, W, Cu, Ag, Pt, Ce, and V proved to be less active. According to the authors,[19] the reaction proceeds with participation of the oxygen from the oxide, as a result of which CH_3 species are formed on the surface of the catalyst, whose interaction leads to the formation of C_2H_6 molecules. Ethane can in its turn undergo oxidative dehydrogenation to ethylene. In order to regenerate the oxide after it has been in contact with methane, it must be treated with O_2-containing gas at the reaction temperature.

Table 1. The activities of certain metal oxides deposited on α-Al_2O_3 in the oxidative condensation of methane to ethane and ethylene at 800 °C[19]

Metal	Conversion of CH_4, %		
	w.r.t. C_2 hydrocarbons	CO_x	total
Initial carrier	0.2	1.6	1.8
Mn	5.0	6.0	11.0
Cd	4.0	6.0	10.0
Sn	0.4	8.0	8.4
Tl	3.0	3.8	6.8
Pb	2.0	2.6	4.6
Bi	0.4	4.0	4.4

The syntheses of C_2 hydrocarbons from methane under conditions where methane, an inert gas, and O_2 are supplied in succession have been proposed in patents.[20–30] Antimony, germanium, bismuth, lead, indium, and manganese oxides deposited on SiO_2 were used as catalysts, which functioned essentially as solid oxidants. At 700–800 °C the conversion of methane and the selectivity in the formation of C_2 hydrocarbons were 0.25–1.06 and 38.5–83.3% respectively. The successive introduction of the reactants into the catalytic zone evidently prevents the attainment of a satisfactory efficiency of the process, although the selectivity with respect to the C_2 hydrocarbons is relatively high.

Hinsen and Baerns,[31–34] investigated the possibility of the oxidative condensation of methane in the presence of O_2 on Pb-, Bi-, Sb-, Sn-, and Mn-containing catalysts. Among these systems, 34 wt.% PbO/γ-Al_2O_3 proved to be the most active catalyst. In its presence at 750 °C and for methane and O_2 contents in the reaction system of 50.9 and 5.2 vol.% respectively, the overall yield of C_2H_6 and C_2H_4 was about 5%. With increase in the PbO concentration in the catalyst, the selectivity in the formation of methane condensation products also increases (Fig.1), which has been attributed to the blocking of the acid centres on the carrier responsible for the extensive oxidation of the hydrocarbons.[34] The surface area of the catalyst also depends on the PbO content, diminishing from 166 $m^2\ g^{-1}$ (for the pure carrier) to 6 $m^2\ g^{-1}$ in the presence of 47 wt.% PbO/γ-Al_2O_3, which is evidently induced by the sintering of the catalyst at the reaction temperature. The influence of the nature of the carrier on the stability of the lead catalysts has been noted.[35] The use of aluminium and titanium oxides makes it possible to obtain systems whose catalytic properties do not change after use for 20–25 h; the lifetime of the SiO_2-based catalyst is significantly shorter, which is due to the loss of lead compounds and the sintering of the catalyst.

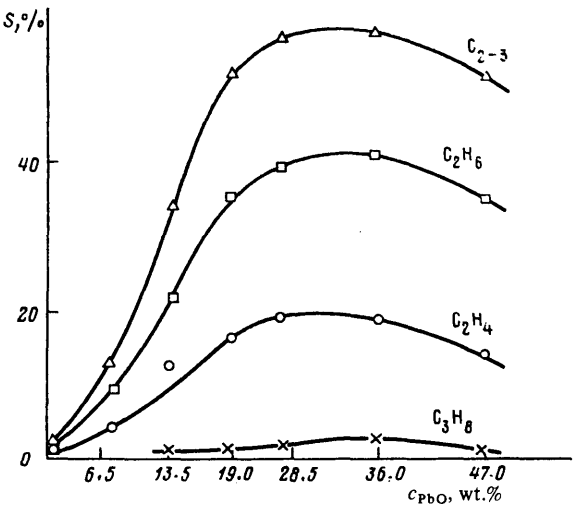


Figure 1. The selectivity S in the formation of the products of the oxidative condensation of methane in the presence of PbO/γ-Al_2O_3 with different contents c_{PbO} of PbO;[80] T = 740 °C; p_{CH_4} = 70.9 kPa; p_{O_2} = 7.1 kPa.

The increase in the process selectivity in the presence of lead systems is promoted by the increase in the reaction temperature and in the CH_4: O_2 ratio.[31] Together with C_2 hydrocarbons, the reaction products contain very small amounts of formaldehyde and propene; the extensive oxidation products were represented mainly by carbon dioxide. Only in the case of Sb_2O_3/SnO and Mn/Al_2O_3, which accelerated mainly the extensive oxidation process, did the selectivity in the formation of CO exceed 5%.[31]

Minachev et al. showed[36,37] that the efficiency of the manganese systems in the oxidative condensation of methane can be significantly increased by replacing the γ-Al_2O_3 carrier by silica gel. In the presence of Mn/SiO_2 containing the optimum amount of manganese in the form of the oxide (10 wt.%), at 750 °C and a volume flow rate ν of the supply of the gaseous mixture of 1000 h^{-1}, and for the CH_4: air = 0.65 molar ratio, the conversion of CH_4 into C_2H_4 + C_2H_6 is 6.3%.[36] The possibility of the oxidative condensation of methane in the presence of Mn/SiO_2 has been confirmed.[38] Although PbO/γ-Al_2O_3 [31] and Mn/SiO_2 [36] have similar activities with respect to the overall yield of C_2 hydrocarbons, they differ appreciably as regards selectivity in the formation

of ethane and ethylene. The $C_2H_4 : C_2H_6$ molar ratio exceeds 1.3 for the manganese catalyst, while for the $PbO/\gamma\text{-}Al_2O_3$ catalyst it is in the range 0.23–0.95. Overall, the composition of the C_2 hydrocarbons formed depends, as will be shown below, not only on the nature of the catalyst but also on the reaction conditions.

The study of the catalytic properties of a large group of pure oxides at 700 °C, for the low $O_2 : CH_4 = 0.022$ molar ratio, and for a high dilution of the reaction mixture with helium (82%) established the following activity series: Sm > Pb > Bi > Ho > Gd > Fr > Tm, Yb, Y > La, Nd, Eu, Dy, Lu, Ca > Zn > Pr, Tb, Ce, Sc, Ge, In, Sn. Under these conditions, the lanthanide oxides exhibit a selectivity with respect to C_2 hydrocarbons greater than 75% and for the most active Sm_2O_3 the selectivity reaches 93%. It is noteworthy that in the presence of Sm_2O_3 the yield of C_2 hydrocarbons does not diminish even after the catalyst has been used for 180 h.[39] The appreciable activity of lanthanide oxides has been confirmed (for Sm_2O_3 and La_2O_3) by a number of data.[40–44] It has been observed that the efficiency of La_2O_3 increases after the addition of alumina[44] and increase in the fraction of the amorphous phase of the catalyst. According to Imai et al.,[44] the active centres for the oxidative condensation of methane are linked to aluminium ions dispersed in La_2O_3.

The ability of systems based on alkaline earth metals to accelerate the synthesis of C_2 hydrocarbons from methane has been demonstrated in a number of studies.[45–50] For the individual magnesium, calcium, strontium, and barium oxides, a steady increase in activity and selectivity with increase in the atomic weight of the metal is observed[45] (Table 2). On passing from MgO to BaO (750 °C), the yield of C_2H_4 and C_2H_6 increases from 4.4 to 15.2%, while the selectivity increases from 11.7 to 45.4%. It has been noted[45] that in the presence of SrO and BaO the reaction products contain no CO_2 during the first hours of the operation of the catalyst, which is associated with the conversion of the oxides into the carbonates. Comparison of the oxide and carbonate catalysts under identical conditions demonstrated the similarity of their properties in the oxidation (Table 2). The possibility of increasing both the activity and the selectivity of the catalyst by a preliminary heat treatment at 1000 °C (Table 2), which reduces the surface of the oxide by a factor of ~4, has been demonstrated for MgO.[48] The catalytic properties of alkaline earth metal oxides are also influenced by other factors, which is indicated by the increase in the activity of MgO after adding a small amount of barium compound (0.2 mole %) (Table 2), which is accompanied by the increase in the surface area of the catalyst from 70 to 200 $m^2\ g^{-1}$.[48]

Thus the oxidative conversion of methane into C_2 hydrocarbons can occur in the presence of a wide variety of oxide catalysts. It is difficult to differentiate any group of metals which is greatly superior in terms of activity and selectivity. Nevertheless, one may note that, with rare exceptions, there are no literature data concerning the use of oxide catalysts containing *d* transition metals, which exhibit a high activity for the extensive oxidation of hydrocarbons.[51,52]

2. Oxide Systems with Added Alkali Metal Compounds

The modifying effect of added alkali metals on catalysts of different processes, including the partial oxidation of organic substances, is widely known.[53] The increase in the activity and selectivity of the catalyst by alkali metals is due to a number of causes, the main ones being the neutralisation of the acid centres of the carrier, the alteration of its adsorption characteristics, the weakening of the bonds between oxygen and the active components, and prevention of coke formation.[53]

Table 2. Catalytic properties of the catalysts of the oxidative condensation of methane containing alkaline earth metals.

Composition of catalyst	Reaction conditions			*B*, %	*S*, %	Refs.
	T, °C	Molar ratio of components	*v*			
MgO	800	$CH_4:O_2 = 5$	0.074 mol $g^{-1}\ s^{-1}$	5.2	50.0	[49]
	900	ditto	*	6.3	70	[47]
	700	$CH_4:O_2:He = 45.5:1:206.8$	—	—	38	[39]
	750	CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	4.4 **	11.7 **	[48]
	750	ditto	ditto	9.0 ***	26.1 ***	[48]
CaO	750	»	»	9.4	28.9	[45]
	800	»	»	12.8	39.1	[45]
	800	$CH_4:O_2 = 5$	0.074 mol $g^{-1}\ s^{-1}$	8.8	72.5	[49]
	700	$CH_4:O_2:He = 45.5:1:206.8$	—	****	70	[39]
SrO	750	CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	10.0	39.0	[45]
	800		ditto	16.3	52.7	[45]
$SrCO_3$	750	ditto	»	8.5	22.7	[45]
BaO	750	»	»	15.2	45.4	[45]
	800	»	»	16.6	44.6	[45]
	800	$CH_4:O_2 = 5$	0.074 mol $g^{-1}\ s^{-1}$	4.3	69.0	[49]
0.2 mole % Ca/MgO	750	CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	4	—	[48]
0.2 mole % Sr/MgO	750	ditto	ditto	4	—	[48]
0.2 mole % Ba/MgO	750	»	»	7.5	—	[48]
40 wt.% BaO/Al_2O_3	700	—	—	5	38	[50]
$BaCO_3$	800	CH_4:air:He = 7.6:1:29.4	64.6 ml min^{-1}	7.1	90.5	[45]
		CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	18.2	48.4	[45]

Notation: *B* is the yield of C_2 hydrocarbons and *S* the selectivity with respect to C_2 hydrocarbons.

* $\tau_{cont} = 0.5$ s.
** Heat treatment at 800 °C.
*** Heat treatment at 1000 °C.
**** Rate of formation 0.2 mol $min^{-1}\ m^{-3}$.

The promoting effect of alkali metal additives on catalysts of the conversion of methane has been observed under conditions where methane and O_2 were supplied consecutively[54–79] and simultaneously.[80–98] For example, when methane came into contact with manganese systems modified by Li, Na, K, Rb, and Cs additives, the yield of the methane oxidative condensation products was higher than for the unpromoted solid carriers.[25,26] The conversion of methane, determined 2 min after the start of the experiment at 800 °C, was 7% in the presence of 10 wt.% Mn/SiO_2 with a selectivity in the formation of hydrocarbons of 55.6%. The addition of 1.7 wt.% Na (as the acetate) to the catalyst increases the conversion of methane and the process selectivity to 9 and 89.9% respectively. It has been noted[37,54] that the efficiency of the manganese systems investigated depends on the nature of the promoting additive and carrier and also on the method of their preparation.

The addition of Na (as sodium nitrite) to PbO/Al_2O_3 in an amount up to 4 wt.% increases the catalyst selectivity by ~10%, while the overall conversion of methane passes through a maximum when the Na_2O content in the catalyst is approximately 2 wt.%[80] (Fig.2). According to Hinsen et al.,[80] the

effect of Na is due to the neutralisation of the acid centres of the carrier, which, as already mentioned, promote the extensive oxidation of hydrocarbons. Accordingly, the promoting effect of added Na is manifested to a greater extent for catalysts prepared on the basis of acid carriers (γ-Al_2O_3, aluminosilicate).[80] The important role of the acid–base properties of the carrier is indicated by results[35] according to which the efficiency of the lead catalyst increases sharply when acid carriers are replaced by alkaline ones (CaO, SrO, BaO, and especially MgO).

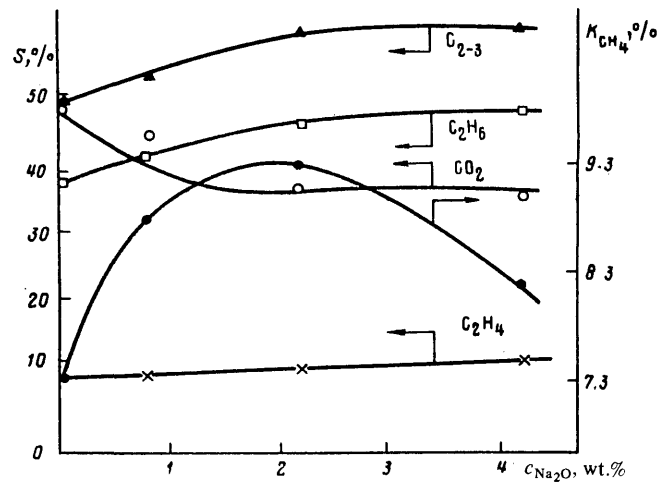


Figure 2. The influence of the alkaline additive on the catalytic properties of the 22 wt.% PbO/γ-Al_2O_3 catalyst in the oxidative condensation of methane;[80] T = 750 °C; p_{CH_4} = 70.9 kPa; p_{O_2} = 7.1 kPa; K_{CH_4} = conversion of methane.

Table 3. Oxidative condensation of methane in the presence of the 10 wt.% Mn/carrier catalyst[37] (T = 750 °C; molar ratio CH_4: air = 0.65; ν = 1000 h^{-1}).

Carrier	K_{CH_4}		S w.r.t. $C_2H_6 + C_2H_4$, %	Molar ratio C_2H_4:C_2H_6
	total	to $C_2H_6 + C_2H_4$		
γ-Al_2O_3	14.9	0.4	2.6	0.08
SiO_2	20.6	6.3	30.6	1.31
NaHSZ (X = 71)*	25.6	13.3	51.9	2.18
NaY (X = 4,4)	17.3	4.1	23.8	1.22
NaA (X = 2)	17.9	3.7	20.7	1.01

*$X = SiO_2/Al_2O_3$ (molar ratio).

The influence of alkaline components must be taken into account when materials such as zeolites, whose composition usually includes Na^+ cations, are used as carriers.[37] The higher efficiency of the Mn/NaHSZ zeolitic catalyst, compared with Mn/SiO_2, is probably associated with this factor (Table 3). The properties of zeolitic catalysts whose structures break up at the methane oxidative condensation temperature (700 to 800 °C) apparently depend also on the aluminium content in the zeolite. With decrease in the SiO_2/Al_2O_3 ratio in the carrier, i.e. with increase in the aluminium content, the yield of the C_2 hydrocarbons falls, although it still remains higher than in the presence of the γ-Al_2O_3-based catalyst (Table 3).

Systematic study of the effect of alkali metal additives on the Mn/SiO_2 catalysts[81] showed that the greatest promoting effect is exhibited by sodium (Table 4). At 800 °C and ν = 2000 h^{-1} in the presence of Mn/SiO_2 containing 4 wt.% Na, the yield of ethane and ethylene reaches 16.9% for a selectivity in the formation of C_2 hydrocarbons greater than 70%. The addition of lithium as the acetate to Mn/SiO_2 also increases the overall conversion of methane (to 25.4%), but the process becomes less selective owing to the increase in the yield of CO_2. Other alkali metals (K and Cs) increase the selectivity of the catalysts but lower their activity. The modification of Mn/SiO_2 by alkaline earth metal (Mg and Ca) compounds reduces appreciably the conversion of methane and the selectivity in the formation of C_2H_4 and C_2H_6 (Table 4). The effect of added alkali and alkaline earth metals on the properties of manganese catalysts[37,81] may be due to the decrease in the acidity of the catalytic systems and also to changes in the valence state of manganese and in the strength of the Mn–O bond.

Table 4. Catalytic properties of 10 wt.% Mn/SiO_2 with added 4 wt.% of alkali metal or alkaline earth metal (M) acetates in the oxidative condensation of methane[81] (T = 800 °C; molar ratio CH_4: air = 0.55; ν = 2000 h^{-1}).

M	K_{CH_4}, %	S, %		B, %	
		C_2H_4	C_2H_6	C_2 hydrocarbons	C_2H_4
—	16.4	41.3	7.3	8.0	6.8
Li	25.4	28.8	14.7	11.1	7.3
Na	23.9	67.5	3.0	16.9	16.1
K	11.3	49.9	13.5	7.2	5.6
Cs	11.2	39.0	14.4	6.0	4.4
Mg	11.5	16.0	11.6	3.2	1.8
Ca	13.5	13.4	10.5	3.3	1.8

The promoting effect of alkali metals has been observed for samarium,[82] zinc,[83] and bismuth oxides deposited on various carriers.[84] The characteristics of the variation of the catalytic properties of Sm_2O_3 and ZnO after the addition of alkali metal (Li, Na, K, Rb, and Cs) compounds are similar. The efficiency of the promoting additive decreases in both cases with increase in the atomic weight of the alkali metal.[82,83] In interpreting the effect of alkali metal additives, one should bear in mind that the promoting agent (Li), deposited on an inert carrier (SiO_2), is inactive in the conversion of methane (Fig. 3). The addition of 20 mole % of Li to Sm_2O_3 makes it possible to convert up to 21% of methane at 750 °C into C_2 hydrocarbons with a selectivity of 57%. This yield of C_2H_4 and C_2H_6 persists in the range of promoting agent concentrations from 10 to 30 mole %, while the maximum selectivity in the oxidative condensation of CH_4 is observed for 5–10 mole %.[82] According to Matsuura et al.,[83] an increase in the activity and selectivity of ZnO is observed when the fraction of Li in the catalyst is increased to 12.5 mole %; further growth of its concentration (up to 40 mole %) does not alter the catalytic properties of ZnO. The highest yield of C_2 hydrocarbons (23.9%) for a selectivity of 66.8% in the presence of Li/ZnO is obtained for a high dilution of the reaction mixture with helium (>80 vol.%) and for the molar ratio CH_4:O_2 = 2.[83]

Important results concerning the nature of the promoting effect of alkali metal additives have been obtained.[85,86] The $[Li^+O^-]$ centres containing active oxygen have been detected by EPR in MgO-based catalysts of the oxidative condensation of methane with added lithium carbonate. These centres are formed only at temperatures above 500 °C in an atmosphere of an O_2-containing gas. Their concentration increases significantly with increase in the partial pressure of O_2 to 13.3 kPa (Fig. 4). According to the authors,[85,86] the $[Li^+O^-]$ centres participate in abstracting H atoms from CH_4 with formation of methyl radicals:

$$[Li^+O^-] + CH_4 \rightarrow Li^+OH^- + CH_3^\cdot .$$

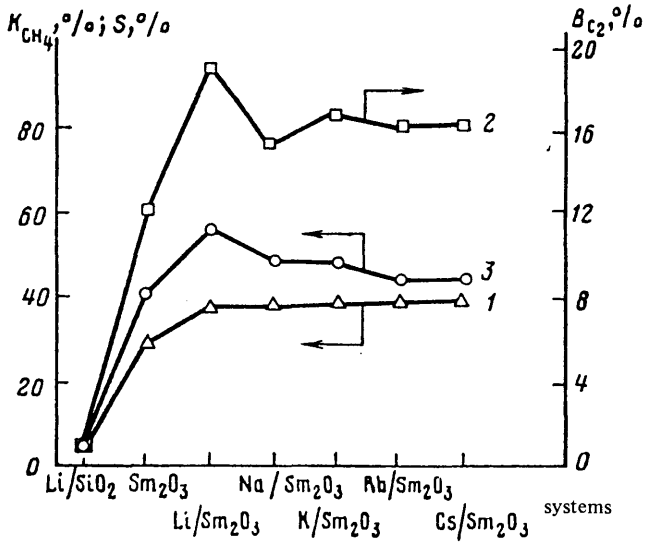


Figure 3. The effect of alkaline additives (20 mole %) on the conversion of methane (curve *1*), the yield *B* (curve *2*), and selectivity (curve *3*) in the formation of C_2 hydrocarbons in the presence of Sm_2O_3 catalysts of the oxidative condensation of methane;[82] T = 750 °C; p_{CH_4} = 5.1 kPa; p_{O_2} = 2.1 kPa; p_{He} = 94.1 kPa.

The $CH_3^\cdot$ radicals are intermediates in the reactions involving the partial and extensive oxidation of methane. The regeneration of the active centres of Li/MgO takes place after the dehydration of Li^+OH^- and the adsorption of O_2, accompanied by the dissociation of the O–O bond. Since these processes are endothermic, they take place at high temperatures.[86] Among the catalysts investigated, the 7 wt.% Li/MgO catalyst proved to be the most active. In its presence at 720 °C and for the molar ratios of the reaction mixture components $CH_4 : O_2 : He$ = 2 : 1 : 23, the yield of C_2 hydrocarbons reached 19% for a selectivity of 50.3%. The Li/MgO system can serve as an example of the direct involvement of the promoting agent (the alkali metal) in the formation of active centres for the oxidative condensation of methane.

According to the data of Moriyama et al.,[87] added sodium nitrate has the greatest promoting effect on MgO, the effect of the nitrates of other alkali metals (Li, K, Rb, Cs) being less marked. In the presence of the catalyst with the optimum composition (15 mole % Na/MgO) at 800 °C and for the volume ratios CH_4 : air : He = 1 : 2.5 : 33.3, C_2 hydrocarbons are formed in 22.4% yield and with a selectivity of 56.8%. The increase in the Na content lowers significantly the thermal stability of the MgO crystal lattice: after heat treatment at 800 °C, the surface area of MgO is 70 $m^2\ g^{-1}$, while for the specimens with 15–20 mole % Na it is only 1–2 $m^2\ g^{-1}$. The authors[87] suggest that the reactions involving the generation of $CH_3^\cdot$ radicals, the extensive oxidation of the hydrocarbons, and the destruction of methyl radicals take place on the catalyst surface. A decrease in the area of the catalytic system retards the last two reactions to a greater extent, which increases the yield of the C_2 hydrocarbons and the process selectivity. The promoting effect of the alkali metal additive is apparently caused, together with other factors, by the modification of the carrier, which leads to the optimum morphology of the catalyst surface.

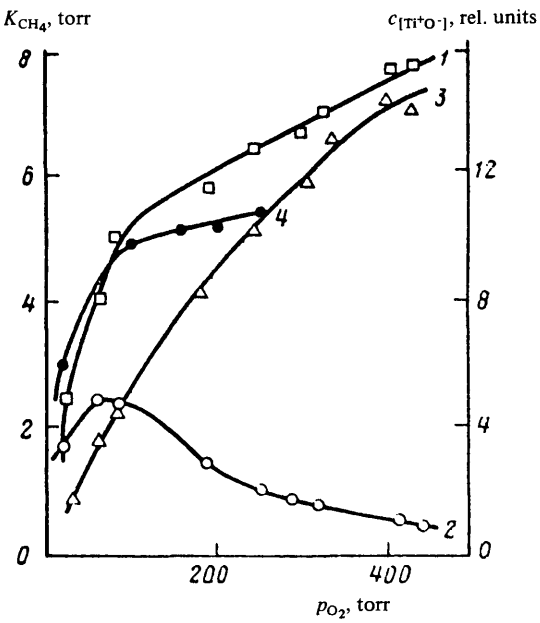


Figure 4. Dependence of the conversion of methane and of the concentration of the $[Li^+O^-]$ centres on the partial pressure of O_2:[86] 1) overall conversion of methane; 2) conversion into $C_2H_6 + C_2H_4$; 3) conversion into $CO + CO_2$; p_{CH_4} = 300 torr; T = 620 °C; catalyst—7 wt.% Li/MgO.

There are literature data[45,88,89] showing that the compounds of other alkaline earth metals (Ca, Sr, Ba) are also sensitive to alkali metal additives. Thus it has been shown that the catalytic properties of MgO and CaO modified with 5 mole % of Li, Na, K, or Cs[88] vary similarly: the yield of C_2H_4 and C_2H_6 and the selectivity in their formation decrease with increase in the ionic radius of the alkali metal (r_{M^+}). These relations have been explained taking into account the results of the X-ray diffraction analysis of the specimens heat-treated at 950 °C. If r_{M^+} is smaller than or equal to the radius of the alkaline earth metal (M^{2+}), then substitutional solutions with healing of the defects in the cationic sublattice are formed. On the other hand, when $r_{M^+} > r_{M^{2+}}$, then M^+ can enter the interstices, which increases the defectiveness

of the MO lattice as far as its conversion into the amorphous form. The latter promotes the adsorption of CO_2 and hence the blocking of the catalyst surface, which reduces its activity.[88] These considerations concerning the role of the conversion of the MO lattice into the amorphous form and the chemisorption of CO_2 in the deactivation of the catalyst differ from the hypotheses put forward by Aika et al.,[45] As already mentioned (Table 2), the formation of $BaCO_3$ from BaO under the conditions of oxidative condensation does not influence the yield of C_2 hydrocarbons, while the addition of Li, Na, K, or Rb compounds to $CaCO_3$ increases somewhat its activity but reduces its selectivity with respect to C_2H_4 and C_2H_6.[45]

On the basis of the data examined, one may conclude that the increase in the efficiency of the majority of catalysts of different nature as a result of the modification by alkali metal additives can be due to a number of causes. In acid systems, their effect is associated with the neutralisation of the acid centres accelerating the extensive oxidation of hydrocarbons. The interaction of alkali metal compounds with the catalysts at high temperatures (700–1000 °C) probably induces various changes in the crystal lattice and in the state of the catalytic surface. This usually leads to the conversion of the catalyst into an amorphous form and its sintering, which ensures the formation of the optimum surface of the catalytic system. Furthermore, alkali metal cations apparently promote the formation of centres containing active oxygen by creating defects and altering the effective charge on the ions localised on the catalyst surface.

Table 5. Catalytic properties of Sm_2O_3 modified by lithium compounds[99] (T = 750 °C; p_{CH_4} = 5 kPa; p_{O_2} = 2 kPa; p_{He} = 94 kPa).

Catalyst	K_{CH_4}, %		S, %	molar ratio $C_2H_4:C_2H_6$
	total	to $C_2H_4 + C_2H_6$		
Sm_2O_3	30.2	12.4	41.2	1.24
$LiBr/Sm_2O_3$	30.4	11.6	38.2	1.98
$LiCl/Sm_2O_3$	28.8	19.9	69.0	5.39
LiF/Sm_2O_3	26.5	13.9	52.6	1.00
$LiOH/Sm_2O_3$	38.2	19.5	51.1	1.09
$LiNO_3/Sm_2O_3$	37.5	19.5	51.9	1.17
Li_2CO_3/Sm_2O_3	41.2	22.3	54.1	0.95

3. Halogen-Containing Catalysts

The study of various catalytic systems promoted by alkali metal salts showed that their catalytic properties depend significantly on the nature of the anion of the added salt.[81,99–102] In the presence of Sm_2O_3,[99] the yield of the oxidative condensation products increases from 12.4% to 19.5–22.3 after the introduction of lithium chloride, hydroxide, nitrate, or carbonate (Table 5). The addition of LiBr and LiF hardly alters the conversion of methane into C_2 hydrocarbons. With the exception of the bromide, lithium compounds increase the selectivity in the formation of C_2H_4 and C_2H_6, the selectivity of $LiCl/Sm_2O_3$ being highest (69%). It is striking that the C_2 hydrocarbons formed in the presence of this catalyst consist mainly (to the extent of 84.4%) of ethylene. The fraction of ethylene in the presence of other catalysts is appreciably lower and is less than 50% for Li_2CO_3/Sm_2O_3. It has been suggested[99] that the observed effects are caused by the suppression of the extensive oxidation of the hydrocarbon by the added LiCl.

The fact that the addition of alkali metal salts to oxide catalysts having different chemical compositions induces similar changes in their activity and selectivity in the oxidative conversion of methane is important for the understanding of the nature of the catalytic action of the systems considered.[81,99,100] Indeed, as for samarium oxide modified by lithium compounds,[99,101] the efficiency of manganese catalysts[81] increases significantly after the introduction of sodium salts into their composition (Table 6). The nature of the halides influences also the proportions of the methane oxidative condensation products (Tables 5 and 6). For example, catalysts modified by LiF and NaF are inferior to other halogen-containing systems as regards selectivity in the formation of C_2H_4. Analogous behaviour has been observed[100] also for NiO + LiX (X = F, Cl, or Br). The addition of lithium and sodium chlorides induces the highest promoting effect; for $(Mn + NaCl)/SiO_2$, the yield of C_2 hydrocarbons reaches 25.8% for a selectivity in their formation of 77.5% (Table 6). The simultaneous increase in the activity and selectivity of the manganese catalyst cannot be explained solely by the suppression of the extensive oxidation of hydrocarbons, as suggested for $LiCl/Sm_2O_3$.[99,100] The Cl^- ions present in the catalyst are probably converted as a result of oxidation-reduction reactions into organochlorine compounds, which accelerate the formation of C_2H_4 and C_2H_6.

Table 6. The influence of the nature of the anion of the added sodium salt on the catalytic properties of Mn/SiO_2 in the oxidative condensation of methane[81] (T = 800°; molar ratio CH_4: air = 0.55; v = 2000 h^{-1}).

Salt	K_{CH_4}, %		S, %	Molar ratio $C_2H_4:C_2H_6$
	total	to $C_2H_4 + C_2H_6$		
—	16.4	8.0	48.6	5.7
CH_3COONa	23.9	16.9	70.5	20.1
NaF	22.3	9.8	43.9	2.9
NaCl	33.3	25.8	77.5	17.4
NaBr	26.8	19.2	71.6	26.4

The change in the catalytic properties of a number of transition metal oxides (Table 7) as a result of their modification by added LiCl has been investigated.[100,101] It must be emphasised that the individual oxides propagated only the extensive oxidation of methane under the selected conditions, while $LiCl/SiO_2$ did not exhibit an appreciable activity in the conversion of methane.[100] The combination of LiCl and metal oxides (with the exception of Fe and Cr) affords effective catalytic systems. Thus, in the presence of LiCl/Mn oxide, the conversion of methane into C_2 hydrocarbons is 30.6% for a selectivity of 64.7%. A high content of C_2H_4 in the methane oxidative condensation product is characteristic of all the catalysts (Table 7) and depends on the partial pressure of the reactants. In the case of LiCl/Mn oxide, the decrease of $p_{CH_4+O_2}$ from 85.5 to 7.65 kPa increases the fraction of C_2H_4 in the C_2 hydrocarbons from 67 to 92% with the simultaneous increase in the overall $C_2H_4 + C_2H_6$ yield by a factor of ~2.[100,101] The importance of the chloride component in the catalytic systems is also indicated by the decrease in the activity of LiCl/NiO with time, which is caused, according to the authors.[100,101] by the removal of LiCl from the catalytic zone. Patent data concerning the possibility of the activation by methylene chloride of the $NaMnO_2/MgO$

solid oxidant used in the cyclic conversion of methane agree with this finding.[103]

The efficiency of alkaline earth metal (Mg and Ca) oxides, in the presence of which the degree of conversion of methane into C_2H_4 and C_2H_6 at 800 °C is ~5%, increases after the addition of LiCl.[100] This is especially notable for the MgO systems: the yield and the selectivity in the formation of C_2 hydrocarbons increase from 4.8 to 19.4% and from 22.4 to 69.7% respectively, i.e. LiCl exhibits simultaneously a promoting effect and suppresses the extensive oxidation of methane. In the case of the oxides SiO_2 and Al_2O_3, which are inactive in the oxidative condensation of methane, the addition of LiCl increases the yield of C_2 hydrocarbons to only 3.6–3.7%.[100] The overall conversion of methane increases by a factor of ~2 (to 26.7%) on passing from Al_2O_3 to $LiCl/Al_2O_3$, mainly as a result of the formation of CO_2. This is the only example of the anomalous influence of LiCl on the catalytic properties of oxide systems in the oxidation reaction of methane.

Table 7. The influence of LiCl (20 mole %) on the catalytic properties of transition metal oxides[101] (T = 750 °C; p_{CH_4} = 5.1 kPa; p_{O_2} = 2.55 kPa; p_{He} = 93.7 kPa).

Metal	K, %		S, %	B, %	
	CH_4	O_2		$C_2H_4 + C_2H_6$	C_2H_4
Ti	17.6	40	82.8	14.6	13.6
Cr	26.1	85	0	0	0
Mn	47.3	95	64.7	30.6	28.1
Fe	22.2	92	0	0	0
Co	48.0	91	35.6	17.0	15.4
Ni	25.9	57	71.8	18.6	14.5
Cu	49.5	80	20.6	10.2	10.2
Zn	22.0	49	68.9	15.2	9.4

The above results[100,101] make it possible to compare the influence of the nature of alkali metals, whose chlorides have been used to modify nickel, samarium, and europium oxides. In the presence of nickel catalysts with 20 mole % MCl (M = Li, Na, or Cs), the yield of C_2 hydrocarbons decreases from 18.6% (Table 7) to 6.2% and to 5.9% with increase in the atomic weight of M. The fraction of C_2H_4 in the methane condensation product diminishes at the same time from 78.0 to 58.0 and to 42.4%, although a parallel variation of the selectivity in the series of these catalysts is not observed. Systems based on Eu_2O_3 and containing LiCl and NaCl hardly differ as regards the yield of C_2H_4 and C_2H_6 but the selectivity of the catalyst with added NaCl is somewhat higher than for the specimen promoted with LiCl. Among the Sm_2O_3 catalysts modified with sodium, potassium, and caesium chlorides, the Na and Cs systems proved to be the most active. The KCl/Sm_2O_3 catalyst exhibits a higher selectivity with respect to C_2 hydrocarbons while being inferior to other Sm_2O_3 systems in terms of the overall conversion of methane (by a factor of ~2). These data show that lithium and sodium chlorides have the greatest promoting effect, although the nature of the carrier also plays a significant role in this case.

Bivalent and tervalent metals [metal halides] deposited on pumices, kieselguhr, and titanium, zinc, magnesium, and calcium oxides can be used as the active components of the halides in the preparation of halogen-containing catalysts of the oxidative condensation of methane.[102] At 750 °C and for the volume ratio CH_4:air = 2:1, $BaBr_2$, $MgCl_2$, $CaCl_2$–$MgCl_2$, $CaCl_2$–LiCl–$CeCl_3$, and $CaCl_2$–LiCl–$PrCl_3$ deposited on pumice exhibit a high efficiency. The yield of the methane condensation products in the presence of these systems is in the range 13–15% for a selectivity of 80–90%. Catalysts which consist of melts of individual salts or mixtures with alkali metal halides (LiCl, CsCl, KBr, and KI) on carriers show a lower activity under the same conditions. The high concentration of C_3 and C_4 hydrocarbons in the methane condensation products obtained in the presence of a series of catalysts with bivalent metal halides is striking. Thus the fraction of butenes is 46.8 and 24.1% respectively in the presence of $BaBr_2$/pumice and $CaBr_2/MgO$. The selectivity of the systems considered with respect to C_3 and C_4 hydrocarbons depends on the nature of the salts and carriers used. For catalysts obtained by depositing $BaBr_2$ on pumice, CaO, ZnO, and silicon carbide, the content of C_3 and C_4 hydrocarbons in the methane condensation products is reduced from 46.8 to 33.9%, which indicates the possibility of regulating the degree of the oxidative condensation of methane by varying the composition of the catalyst.

Thus the efficiency of halogen-containing catalysts in the oxidative condensation is greater than that of other catalytic systems. The promoting function of the halide components is due to a number of factors. Their involvement in the formation of intermediates in the oxidative condensation of methane and in the suppression of processes involving the extensive oxidation of hydrocarbons appears to be extremely probable. The latter factor is indicated, in particular, by the results of studies of the deactivation by the chloro- and bromo-derivatives of methane and ethane of palladium and platinum catalysts of the extensive oxidation of methane.[104] These chloro- and bromo-derivatives are adsorbed preferentially on the centres responsible for the activation of oxygen reacting with methane. Additional evidence in support of the concept of the inhibition of the extensive oxidation of hydrocarbons is provided by data indicating a sharp change in the selectivity of the oxides of a series of transition metals in the oxidation reaction of methane after the addition of halide salts, which leads to the preferential formation of the products of the oxidative condensation of methane. On the other hand, these systems are more effective than non-transition metal halides deposited on inert carriers, which indicates the interaction of the halide component with transition metal compounds under the catalytic conditions. Such interaction apparently induces the formation of active halogen species promoting the condensation of methane. This agrees with the decrease in the activity of the catalysts as a result of the loss of the halide component and the possibility of an increase in their activity following the addition of volatile halogen compounds to the reaction mixture. A high content of ethylene in the C_2 hydrocarbon formed is characteristic of the catalysts considered, i.e. the presence of halogens influences different stages of the catalytic process, including the stages responsible for the appearance of different proportions of the methane condensation products.

III. THE MECHANISM OF THE OXIDATION REACTIONS OF METHANE

Comparison of the properties of catalysts of different classes makes it possible to discover a series of common features of the oxidative condensation of methane. The most important factor is that C_2 hydrocarbons are formed in the presence of all the catalysts only at temperatures above 550–600 °C. Fig. 5 presents typical temperature variation of the yield of the products of the extensive and partial

oxidation of methane in the presence of a manganese catalyst.[37] Up to 600 °C, the only products are carbon oxides and water and under these conditions the oxygen in the gas mixture is almost fully converted (to an extent greater than 95%). At higher temperatures, the formation of C_2H_6 and C_2H_4 is observed, their yield increasing up to 800 °C. At the same time there is an increase in the selectivity with respect to the C_2 hydrocarbons and the oxidative condensation of methane becomes the dominant process at temperatures above 750 °C. It is noteworthy that, in the presence of Mn/NaHSZ at 700–800 °C, ethylene is formed in greater amounts than ethane, which may be associated with the increase in the rate of dehydrogenation of ethane on passing to high temperature.

The character of the oxidative conversion of methane is determined, apart from reaction temperature, by the contact time and the ratio of the components of the reaction mixture.[37,80,83,105] The kinetic relations (Fig. 7*a*) obtained for low conversions of O_2 on Sm_2O_3 [105] show that the selectivity with respect to C_2 hydrocarbons increases steadily with decrease in p_{O_2} and approaches 100% for $p_{O_2} < 0.3$ kPa. The increase in the selectivity in the oxidative condensation of methane and in the rate of formation of the methane conversion products is favoured by an increase in p_{CH_4} (or in the ratio $CH_4:O_2$), which is clearly manifested in the range of p_{CH_4} from 0 to 30 kPa (Fig. 7*b*).

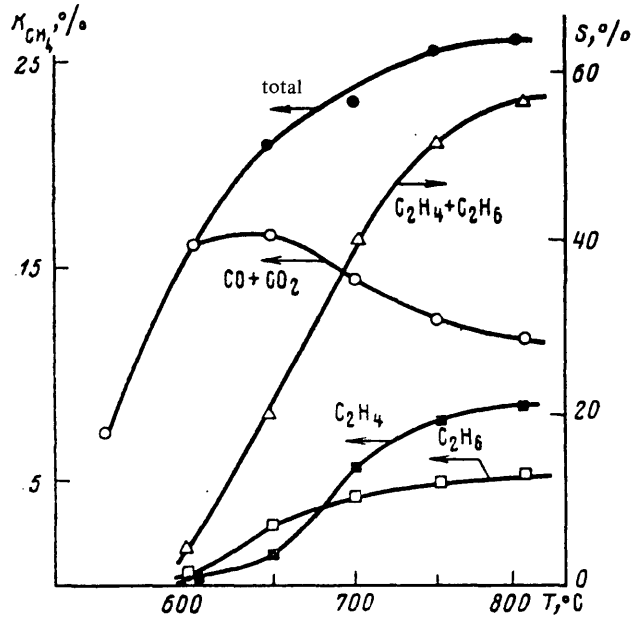


Figure 5. The influence of temperature on the yield of the products of the oxidation reactions of methane:[81] 10 wt.% Mn/NaHSZ ($X = 71$); molar ratio CH_4:air = 2:3; ν = 1000 h^{-1}.

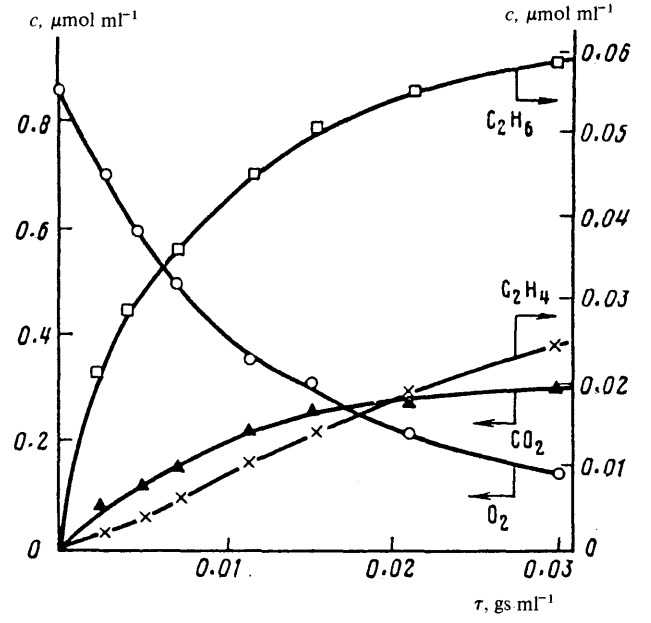
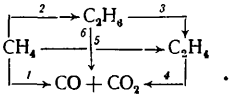


Figure 6. Dependence of the yield of the products of the oxidative condensation of methane on the contact time τ on PbO/γ-Al_2O_3;[80] T = 700 °C; c_{CH_4} = 5.0 mol ml^{-1}; p_{CH_4} = 40 kPa.

It has been shown for the PbO/γ-Al_2O_3 [80] and Li/MgO [86] catalysts that an increase in the contact time τ leads to an increase in the yield of the products of the extensive and selective oxidation of methane. In the presenece of the lead system (Fig. 6), the yield of ethylene varies linearly over the entire range of values of τ and the conversion of CH_4 into C_2H_6 after long contact times tends to a limit. This increases the ratio C_2H_4/C_2H_6, indicating the consecutive formation of C_2H_4 from C_2H_6. It has been noted for Li/MgO [86] that the curves for the formation of the methane oxidation products at 620 °C do not pass through the origin of coordinates. Since diffusion-dependent obstacles are unlikely on Li/MgO in view of the low surface area of the catalyst (2 m^2 g^{-1}) and the absence of micropores, the authors[86] attribute the observed variation to the possibility of the reaction of methane via a chain mechanism.

The composition of the products formed as a result of the extensive oxidation and the oxidative condensation of methane suggests a mechanism reflecting the following possible reactions of the hydrocarbons:



The contribution of the individual reactions to the overall processes can be inferred from data obtained in studies[86,105] of the reactions of individual hydrocarbons under the conditions of the oxidative condensation of methane. The results of experiments on the oxidation of CH_4, C_2H_6, and C_2H_4 in the presence of Sm_2O_3 are presented in Table 8. The initial C_2H_6 and C_2H_4 partial pressures correspond to the pressures of these substances in the mixture obtained on oxidation of methane. Evidently the main bulk of CO and CO_2 is formed as a result of the direct oxidation of methane (see Scheme

above, reaction 1), which is consistent with data for Li/MgO, in the presence of which the yield of CO and CO_2 in the oxidation of methane is greater by a factor of 3.6 than in the oxidation of ethane. The fact that the CO and CO_2 partial pressures are somewhat smaller in the oxidation of C_2H_4 (Table 8) than in the oxidation of C_2H_6 indicates a greater involvement of ethane in the extensive oxidation reaction (reaction 5) than that of ethylene (reaction 4).

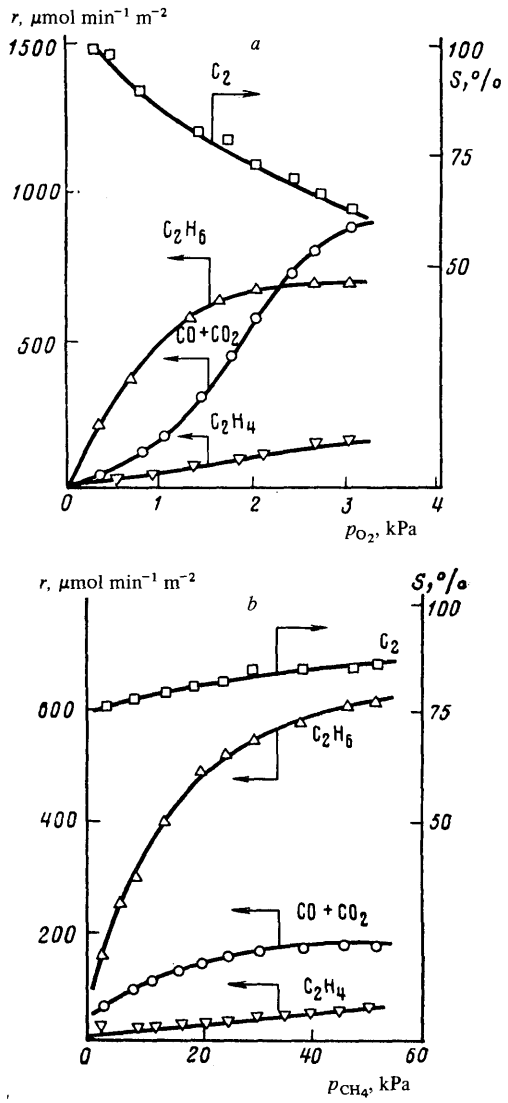


Figure 7. The influence of the partial pressures of O_2 (*a*) and CH_4 (*b*) on the rate of formation of the products of the oxidative conversion of CH_4 (*r*) and on the selectivity with respect to C_2 hydrocarbons;[105] catalyst—Sm_2O_3; T = 700 °C; p_{CH_4} = 18.2 kPa; p_{O_2} = 0.98 kPa.

Comparison of the rates of formation of C_2H_4 from CH_4 and C_2H_6 (Table 8) shows that they differ little, i.e. that C_2H_4 is formed from ethane—the primary product of the oxidative condensation of methane, and not via reaction 6 (see Scheme).

Table 8. The partial pressures of the methane oxidation products over Sm_2O_3 [105] (T = 710 °C; mass of Sm_2O_3 = 3.3 mg; v = 37.5 ml min^{-1}).

Initial hydrocarbon	Partial pressures of compounds, kPa					
	O_2	CH_4	C_2H_6	C_2H_4	CO_2	CO
CH_4	$9.2\cdot10^{-1}$	7.7	$1.2\cdot10^{-2}$	$1.6\cdot10^{-4}$	$1.1\cdot10^{-2}$	$0.2\cdot10^{-3}$
C_2H_6	$9.2\cdot10^{-1}$	0	$1.3\cdot10^{-2}$	$2.0\cdot10^{-4}$	$9.5\cdot10^{-4}$	$2.4\cdot10^{-4}$
C_2H_4	$9.2\cdot10^{-1}$	0	0	$2.0\cdot10^{-6}$	$6.4\cdot10^{-6}$	0

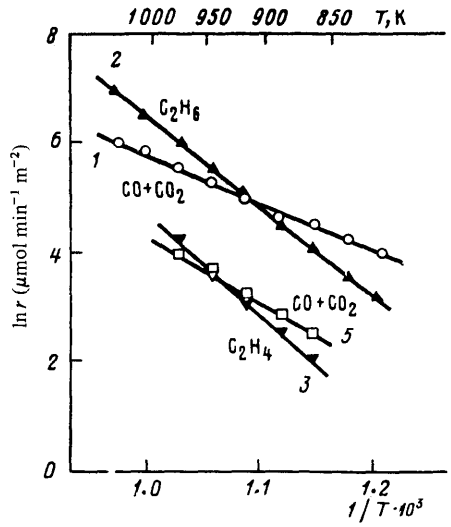


Figure 8. The Arrhenius relations for the extensive and selective oxidation reactions of CH_4 (lines *1* and *2*) and C_2H_6 (lines *3* and *5*) in the presence of Sm_2O_3 [105] (the numerals correspond to the numbers of the reactions presented in the Scheme); p_{CH_4} = 18.2 kPa; p_{O_2} = 0.98 kPa.

The apparent activation energies E_{act} calculated from the data in Fig. 8 [105] for the extensive oxidation of CH_4 and C_2H_6, the oxidative condensation of CH_4 to C_2H_6, and the oxidative dehydrogenation of C_2H_6 to C_2H_4 in the presence of Sm_2O_3 are respectively 66, 94, 135, and 173 kJ mol^{-1}. The higher values of E_{act} for the formation of C_2H_6 and C_2H_4 compared with E_{act} for the extensive oxidation of hydrocarbons show that an increase in temperature promotes the selective conversion of methane into C_2 hydrocarbons. An important factor is that such differences have been discovered for a whole series of catalysts containing lead,[80] barium, cadmium, tin, antimony, and thallium[89,106] oxides. Under comparable conditions, the E_{act} for the selective conversion of methane are within a narrow range of values for catalysts of different chemical nature. Consequently, the mechanism of the formation of C_2 hydrocarbons can include stages characteristic of a wide range of catalytic systems, for example, the formation of CH_3 radicals on the surface of the catalyst and their transfer to the gas phase.[86] The heterogeneous-homogeneous mechanism is supported by the similarity of the E_{act} for the formation of C_2 hydrocarbons and methyl radicals,[89,106] whose existence has been confirmed by EPR.[47,107]

The important role of the $CH_3^{\bullet}$ species in the oxidative conversion of methane is indicated by data for isotope exchange between CD_4 and CH_4 in the presence of oxide catalysts.[84,108] It was found that only one hydrogen atom exchanges in the adsorption–desorption cycle of the CH_4 molecule, which has been explained by the dissociative reaction of CH_4 on the surface of the oxide with formation of the $CH_3^{\bullet}$ and $H^{\bullet}$ species. The removal of hydrogen is facilitated by the formation of C_2H_6 from the $CH_3^{\bullet}$ radicals, so that the active catalyst should combine, according to the authors,[84] the functions ensuring the dissociation of CH_4 and the oxidation of $H^{\bullet}$.

Nowadays the majority of investigators believe that the active centres of the oxide catalysts on which the $CH_3^{\bullet}$ species are generated contain oxygen in one state or another.[86,105,109,114] Thus the formation of $CH_3^{\bullet}$ radicals is regarded[109] as a result of the interaction of CH_4 with the oxygen in the crystal lattices of the oxides. This conclusion is based on the fact that the amount of oxygen incorporated in the reaction product after CH_4 has been in contact with the solid oxidant exceeds the amount of oxygen in the surface layer by a factor of 10–20, i.e. the oxygen present in the bulk of the oxide enters into the reaction. Under the catalytic conditions, the main bulk of the $CH_3^{\bullet}$ radicals are probably formed with participation of the oxygen in the surface layer of the oxide, whose loss is made good by the O_2 from the gas phase. As already mentioned, the active centres in Li/MgO [86] are regenerated by the reaction of O_2 with the structural defects in MgO. This induces the appearance of the coordination-unsaturated O^- species, whose concentration is correlated with the content of Li^+ in the catalyst and with the rate of formation of the $CH_3^{\bullet}$ radicals (Fig. 4).

Another state of active oxygen has been detected on La_2O_3 after its treatment in an atmosphere of an O_2-containing gas at 650 °C and rapid cooling to −196 °C.[43] The EPR spectra of the oxide contained lines whose g-factors ($g_{\parallel} = 2.047$, $g_{\perp} = 1.994$) are characteristic of the superoxide ion O_2^-. The conclusion that diatomic oxygen species (O_2, O_2^-, or O_2^{2-}) participate in the dissociation of the C–H bond in the CH_4 molecule was reached[111,112] on the basis of kinetic studies of the oxidative condensation of CH_4 in the presence of Sm_2O_3. This agrees with the finding that the peroxides Na_2O_2, SrO_2, and BaO_2 are capable of oxidising methane to C_2 hydrocarbons at relatively low temperatures (200–450 °C).[113,114] The interaction of methane with the peroxide oxygen in Na_2O_2 involves the surface and deep layers of the Na_2O_2 lattice, which is indicated by the ratio of the oxygen in the reaction products and in the outer layer of the oxidant.[113] Comparison of the apparent E_{act} for the oxidative condensation of methane (59 kJ mol^{-1}) and decomposition of BaO_2 (142–192 kJ mol^{-1}) indicate the involvement of the peroxide ions O_2^{2-} in the reaction and not of the gaseous O_2 formed on thermal dissociation of BaO_2 [89,114] Thus the state of the active oxygen can be influenced by the nature of the promoting agent and the oxide employed. At the same time, for a number of catalysts, for example, those which contain chlorides, one cannot rule out the generation of the $CH_3^{\bullet}$ radicals when methane interacts with the halide components of the reaction system.[81,100]

The question of the site where the methyl radicals recombine has been confirmed in a number of investigations.[16,19,86,106] It has been suggested[19] that ethane is formed as a result of the dimerisation of the $CH_3^{\bullet}$ species on the surface of the solid oxidant with subsequent dehydrogenation of the adsorbed C_2H_6 to C_2H_4. Another view has been expressed[109] on the basis of kinetic data obtained in the cyclic oxidation of methane in the presence of Mn/SiO_2 (Fig. 9). Extrapolation of the relations presented shows that the selectivity in the formation of all the products (with the exception of ethane) tends to zero with decrease in contact time. The increase in the selectivity with respect to C_2H_6 under the given conditions has been explained[109] by the gas-phase interaction of the $CH_3^{\bullet}$ radicals, because strong adsorption of these species on the Mn/SiO_2 surface should also lead to the formation of C_2H_4 and the extensive oxidation products.

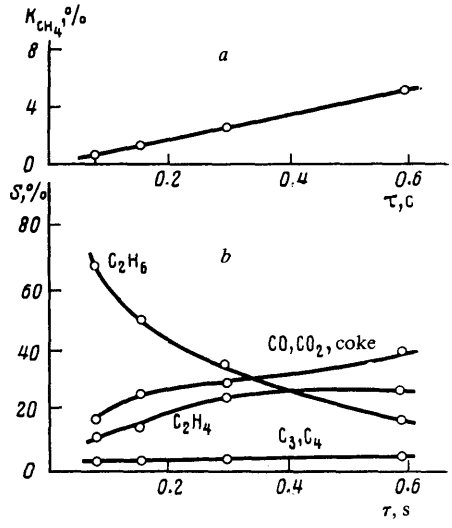


Figure 9. Dependence of the degree of conversion of methane and of the selectivity in the conversion process on the time of contact with the solid oxidant 5 wt.% Mn/SiO_2 at 800 °C [109] (data obtained 1 min after the start of the experiment).

The conclusion that the gas-phase dimerisation of the $CH_3^{\bullet}$ radicals takes place has also been reached by other investigators[86,106] who studied the catalytic conversion of methane in the presence of gaseous oxygen. According to the mechanism proposed,[86] after their appearance on the surface, the $CH_3^{\bullet}$ radicals pass to the gas phase, where they form C_2H_6. The methyl species can also interact with oxygen, affording the methylperoxy-radicals $CH_3O_2^{\bullet}$, which are intermediates in the extensive oxidation reaction. This agrees with the increased yield of CO and CO_2 following an increase in the partial pressure of O_2 [37,83,105] and also with the finding that the main bulk of carbon oxides are formed from methane under the conditions of the oxidative condensation of methane and not from C_2H_6 or C_2H_4 [86,105] (Table 8). It is noteworthy that the $CH_3O_2^{\bullet}$ species are fairly stable up to ~500 °C, as has been established in the gas-phase oxidation of methane by oxygen.[116] The decrease in the O_2 concentration and the increase in temperature therefore promote the decomposition of $CH_3O_2^{\bullet}$ into O_2 and $CH_3^{\bullet}$, which leads ultimately to an increase in the selectivity with respect to C_2 hydrocarbons.[43] The gas-phase oxidation is probably not the only pathway to the formation of CO and CO_2 under the conditions of the catalytic conversion of methane. The heterogeneous occurrence of the extensive oxidation process is indicated by the large amount of carbon oxides formed in the reaction of CH_4 with the solid oxidant in the presence of gaseous oxygen.[109] Lunsford and co-workers[86] assumed that extensive oxidation includes the interaction of the $CH_3^{\bullet}$ radicals with the O^{2-} ions

of the catalyst. Unfortunately there are insufficient data to infer the nature of the surface intermediates and the centres responsible for their extensive oxidation.

Together with the generation of the $CH_3^{\cdot}$ radicals and the formation of carbon oxides, the oxidative dehydrogenation of ethane can be attributed to reactions occurring on the surfaces of the catalysts. This is indicated indirectly by numerous data (see Section II) for the dependence of the C_2H_4/C_2H_6 ratio on the composition of catalysts used under identical conditions. In particular, the introduction of dehydrogenating additives (ZnO, NiO) into PbO/Al_2O_3 increases the fraction of ethylene in the products of the oxidative condensation of methane.[115] It has been suggested[89] that, when PbO/Al_2O_3 is used, ethane is formed from methane and ethylene is formed from ethane (in contrast to the extensive oxidation reaction) on the same active centres. According to Ito et al.,[86] the first stage in the dehydrogenation of C_2H_6 in the presence of Li/MgO takes place with participation of O^- ions and the $C_2H_5^{\cdot}$ radicals formed in this process are converted into C_2H_4 under the influence of the O^{2-} anion in the oxide lattice. As shown in the previous Section, the fraction of ethylene in the C_2 hydrocarbons formed in the presence of halogen-containing catalysts is much greater than in the presence of oxide systems. It has been suggested[100] that the dehydrogenation of C_2H_6 is accelerated in the gas phase by the $Cl^{\cdot}$ radicals, although this has not so far been confirmed directly.

Data indicating the formation of hydrocarbons containing three and more carbon atoms together with C_2H_6 and C_2H_4 are of undoubted interest both from the standpoint of the elucidation of the nature of the reactions occurring in the oxidative condensation of methane and from the practical point of view. C_3 and C_4 hydrocarbons are most frequently detected when the methane conversion is carried out under cyclic conditions.[109] Kinetic investigations have shown[109] that the increase in the duration of contact between methane and the solid Mn/SiO_2 oxidant increases the content of ethylene, propene, and butenes and reduces the fraction of ethane in the methane condensation products (Fig.9), which indicates the successive formation of C_2–C_4 olefins from C_2H_6. Furthermore, the yield of C_3H_6 and C_4H_8 increases appreciably when ethylene and propene are added respectively to methane. Hence it follows that the degree of the oxidative condensation of methane is controlled by the intensity of the reactions between the olefins formed and the $CH_3^{\cdot}$ radicals.[109] The absence of appreciable amounts of C_3 and C_4 hydrocarbons under the catalytic conditions may be associated with the high concentration of oxygen in the gas phase and on the catalyst surface, which promotes the extensive oxidation of these hydrocarbons and the intermediates involved in their formation. It may be expected that further study of the mechanism of the oxidative reactions in the CH_4–O_2–catalyst system will yield new results elucidating further the synthetic possibilities of the oxidative condensation of methane.

The solution of the problem of the activation of methane and of its selective conversion into valuable products is of fundamental and practical importance. The steadily increasing stream of information about the direct synthesis of C_2 and other hydrocarbons from methane shows that, in essence, a new field has been established in the chemistry of methane. There is no doubt that the practical application of the oxidative condensation of methane still requires the solution of a number of complex theoretical and applied problems. The improvement of the catalytic conversion of methane is associated in the first place with a deeper understanding of the reaction mechanism, of the nature of the active centres in the catalytic systems, and of their deactivation processes. However, considerable advances have already been made in the development of effective catalysts and in the selection of optimum conditions for the oxidative condensation of methane.

In the presence of the most active and selective catalysts, methane can be converted to the extent of 40% in a single pass with a selectivity of 70–80% with respect to C_2 hydrocarbons.[81,116] It is important that such results have been obtained for mixtures with high concentrations of the starting materials and at high volume flow rates. In many cases the C_2 hydrocarbons contain up to 95 vol.% of ethylene, which is of exceptional interest in connection with the steadily growing requirements for this product, whose world production will reach ~45 million tonnes according to predictions for 1990.[117]

The preparation of ethylene from natural gas will reduce the consumption of the petroleum raw material in this industry. Furthermore, the ethylene formed by the oxidative conversion of methane, can be almost fully converted, without being isolated from the gaseous mixture, into other olefins and aromatic hydrocarbons[118] in the presence of zeolites of the pentasil type.[7] Thus the oxidative condensation of methane opens a pathway to the synthesis of various compounds which are currently obtained by the processing of petroleum. The role of such processes will probably increase greatly in the future, because any depletion in the available resources of methane can be made good by the biochemical decomposition of a wide variety of organic substances.

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The Reactions of Compounds with Halogenoimidoyl Groups

T.D.Petrova and V.E.Platonov

New data on the reactions of compounds of different classes containing the halogenoimidoyl group -N = C-Hal, including the reactions of both the halogen atom and the N = C bond, are surveyed.
The bibliography includes 310 references.

CONTENTS

I. Introduction 234
II. Nucleophilic substitution at the N = C bond 234
III. Elimination reactions 240
IV. Addition reactions 243

I. INTRODUCTION

The reactions of compounds with halogenoimidoyl groups $-N=\overset{|}{C}-Hal$ are extremely varied. The high mobility of their halogen atom and the ability of the N=C bond to enter into various reactions determine the possibility of using these compounds as precursors of derivatives of almost any type, including heterocyclic compounds. The ability to serve as sources of reactive intermediate ions extends still further their synthetic possibilities. It is therefore not surprising that reviews and monographs have been devoted to the study of these reactions.[1-3] However, after 1970, data for only individual types of compounds, in particular imidoyl fluorides and difluorides as well as fluorinated imidoyl halides,[4-6] hydrazonohalides, and halogenoazines[7-9] have been treated systematically. Some information about other compounds with halogenoimidoyl groups can be found in a series of comparatively recently published monographs[10-14] and reviews (1971–1973),[15-17] but they are not complete.

It appeared useful to give a systematic account of the extensive data on the reactions of compounds with the $-N=\overset{|}{C}-Hal$ groups published after 1970 and not included in the publications quoted above. This attempt was made in the present review. Bearing in mind the available review articles on the reactions of imidoyl difluorides and fluorides, only new data obtained in recent years are included. In the case of hydrazonohalides and halogenoazines, attention has been concentrated on studies after 1974 and 1977 respectively. Only a few examples of the reactions of compounds in which the halogenoimidyl group enters into the composition of a heterocycle or is attached to a heterocycle are presented. All the information about the reactivity of compounds with halogenoimidoyl groups has been divided into three groups corresponding to three main types of reactions: nucleophilic substitution reactions at the N=C bond, elimination reactions, and addition reactions. A common feature of these reactions is that they frequently do not stop after the formation of the primary products but proceed further and lead to a wide variety of final compounds, including heterocyclic derivatives.

Only the chemical reactions of compounds with halogenoimidoyl groups are considered in this review. New data on some of their other properties can be found in other publications: ^{13}C and ^{15}N NMR spectra,[18-20] IR and Raman spectra,[10] data on the dipole moments, configurations, and conformations,[10,21-24] and quantum-chemical calculations.[10,25-28]

II. NUCLEOPHILIC SUBSTITUTION AT THE N=C BOND

In terms of its properties (bond length and bond energy, dipole moment), the N=C bond occupies an intermediate position between the C=O and C=C bonds. The reactions with nucleophiles have been investigated fairly adequately for activated vinyl halides and acyl halides, but simple azomethine systems have been investigated to a much lesser extent. However, by analogy with nucleophilic reactions of the C=O and C=C bonds, one can assume that nucleophilic attack on the N=C bond should lead to the formation of an anion or zwitter-ion, which can subsequently give rise to substitution, addition, and cleavage products. In halogenoimidoyl compounds there is in addition the possibility of the dissociation of the C–Hal bond and the formation of cationoid intermediates, which are also capable of undergoing various reactions.

1. Reactions with O-Nucleophiles

(a) Hydrolysis

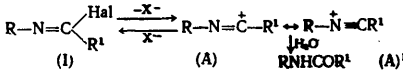
The hydrolysis of imidoyl halides with formation of amides is characteristic of compounds of this class.[29-39] Many imidoyl halides are extremely sensitive even to atmospheric moisture, as a result of which their isolation in a pure form is difficult and their formation in the course of reaction is inferred from the amide isolated. On the other hand, a convenient preparative method of synthesis of amides has been based on this finding.[40] However, this mode of the reaction is not unique. Thus the products of the hydrolysis of chloroformamidines are the corresponding ureas.[34,41-44] The hydrolysis of *N*- arylchloroformimidates or the corresponding chlorothioformimidates can lead to carbamates or their decomposition products—anilines, hydroxy-derivatives, and CO_2.[34] The hydrolysis of *N*-arylcarboimidoyl dichlorides takes place with formation of amino-derivatives of carbamates.[45] 4-Aminotetrachloropyridine is the only product of the acid hydrolysis of *N*-(2,3,5,6-tetrachloro-4-pyridyl)carboimidoyl dichloride.[46] *N*-(trichloromethyl)carboimidoyl dichloride reacts with water vigorously in a solvent or on heating until the decomposition is complete.[15]

At the same time, the reactions of imidoyl halides with water do not always take place readily. Thus certain *N*-(pentafluorothio)chloroformimidates and the corresponding chloroformamidines proved to be fairly resistant to hydrolysis.[47] *N*-(Pentafluorophenyl)halogenoacetimidoyl chlorides

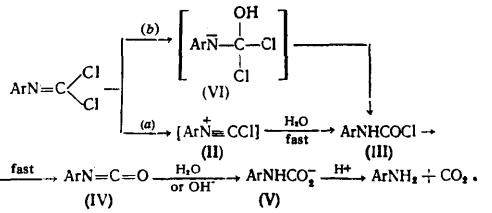
hardly interact with water even on being boiled.[37] Perfluoroalkylimidoyl iodides also do not hydrolyse under mild conditions.[48] Their conversion into the corresponding amides requires refluxing with 20% hydrochloric acid.

The hydrolysis of halogenoazines can afford various products, including ylidene hydrazides and heterocyclic derivatives, depending on their structure and the hydrolysis conditions.[8,49-52] On treatment with water, hydrazonohalides are converted into the corresponding hydrazides of cyclic products.[7,53-60]

The mechanism of the hydrolysis of compounds with halogenoimidoyl groups has so far been studied fairly completely. Kinetic studies on imidoyl chlorides and dichlorides,[34,45,61] halogenoazines,[8,51,62] and hydrazonohalides[8,55-58] have shown that the unimolecular S_N1 mechanism with the dissociation of the C–Hal bond as the rate-determining stage is most characteristic of the hydrolysis of these compounds. The nitrilium ion (A), for which the contribution by the octet resonance structure (A)[1] predominates, is then formed as an intermediate:

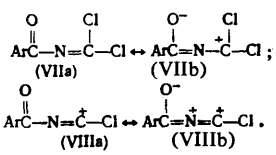


However, this mechanism is not unique and can vary depending on the structure of the substrate, the reagent, and the medium. Thus the hydrolysis of *N*-arylcarboimidoyl dichlorides (I, R = Ar, R^1 = Cl) in solution in the 1:4 dioxan–water mixture at 25 °C and a pH of the medium up to approximately 12 is characterised by the Hammett constant $\rho = -2.30$, which indicates the operation of the S_N1 mechanism via the intermediate nitrilium ion (II) (pathway *a*):



This results in the formation of the carbamoyl chloride (III), which is rapidly converted into the isocyanate (IV). The addition of water to the latter and the decomposition of the resulting carbamate (V) gives rise to the observed reaction products.[45] As the concentration of OH^- ions increases, there is a direct attack by the hydroxyl on the substrate (pathway *b*) with formation of the tetrahedral intermediate of type (VI) (S_N2 mechanism, $\rho = +1.26$). The observed influence of the substituents in the arene ring on the rate of hydrolysis confirms the above findings.

The hydrolysis of *N*-aroylcarboimidoyl dichlorides (I, R = COAr, R^1 = Cl) takes place 10^3 times faster under similar conditions, although the rate via the S_N1 mechanism diminishes by a factor of 10^6. Only the bimolecular mechanism operates. The observed facts can be accounted for by the greatest sensitivity of *N*-aroylcarboimidoyl dichlorides to nucleophilic attack [see the structure (VIIb)] and also by the stabilisation of their negative charge adjoining the carbonyl group in the type (VI) intermediate and the destabilisation of the nitrilium ion postulated for the S_N1 mechanism [see the structure (VIIIb)]:[45]

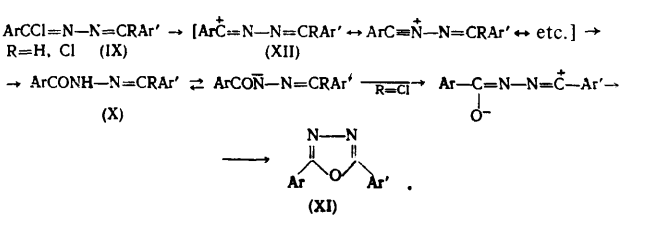


In aqueous dioxan, the hydrolysis of *N*-aryl- and *N*-aroylbenzimidoyl chlorides in the corresponding chlorothioimidates and chloroformamidines (I, R = Ar or COAr, R′ = Ar′, SAr′, or NMeAr′, Hal = Cl) proceeds via the S_N1 mechanism. Under these conditions, *N*-arylimidoyl chlorides are 10^6 times more reactive. On the other hand, the bimolecular mechanism of the hydrolysis reaction is more characteristic of the corresponding chloroformimidates (I, R = Ar or COAr, R′ = OAr′, Hal = Cl) under similar conditions.[35,45] The tendency of *N*-arylchloroformimidates to hydrolyse via the S_N2 mechanism, in contrast to other *N*-arylimidoyl chlorides, is attributed to the influence of substituents at the imidoyl carbon atom on the formation and stabilisation of the developing carbonium centre, which varies in the sequence Ar > NMeAr > SAr > OAr. Compared with the sulphur atom, the oxygen atom stabilises the carbonium centre to a lesser extent owing to the mesomeric effect and destabilises it more because of the greater negative inductive effect. In all cases, the degree of cooperation with the formation of the carbonium centre as a result of the delocalisation of the positive charge is greater for the aromatic ring linked to the nitrogen atom than for that linked to the carbon atom, because the contribution of the octet resonance structure to the nitrilium ion predominates.

The S_N1 mechanism has been established for the hydrolysis in aqueous dioxan of the isomeric (*Z*)- and (*E*)-*O*-methylbenzohydroximoyl halides,[33] the (*Z*)-isomers hydrolysing almost 470 times faster than the (*E*)-isomers. This shows that the free electron pair at the nitrogen atom should be preferentially in the *trans*-position with respect to the leaving group in the formation of the intermediate nitrilium ion. The nature of this group affects the rate of hydrolysis. For bromine, the rate is much higher than for chlorine, which also confirms the S_N1 mechanism.

Compared with *N*-arylimidoyl halides, *O*-methylbenzohydroximoyl halides hydrolyse with more difficulty (at 120 °C compared with room temperature for imidoyl halides), which can be explained by the destabilisation of the intermediate nitrilium ion by the electronegative methoxy-group at the nitrogen atom.

It follows from kinetic data for the hydrolysis in an aqueous organic medium of halogenoimidoyl groups in halogenoazines[8,50,51] that for compounds of this type the mechanism can change, as for imidoyl halides, from the dissociative S_N1 mechanism to the associative S_N2 mechanism depending on the structure of the substrate and the medium. For example 1,4-diaryl-1-chloro, and 1,4-diaryl-1,4-dichloro-2,3-diazabuta-1,3-dienes (IX, R = H or Cl) are converted respectively into the hydrazides (X) and the oxadiazoles (XI) in aqueous dioxan; a similar slow stage, involving the unimolecular cleavage of the C–Cl bond and the formation of the stabilised nitrilium ion (XII), has been observed for compounds of both series:



In basic media, compounds of both series are subjected to direct S_N2 attack by hydroxide, but only provided that electron-accepting substituents are present in the arene rings. In other cases, the rate of reaction falls with increase in the concentration of OH^- ions.[50]

In the series of hydrazonohalides, studies have been made of the kinetics of the hydrolysis in an aqueous organic medium of *N*-arylhydrazonobromides[55-57] and *N*-amidinohydrazonobromides,[58] including those with the amidine group as part of the composition of the heterocycle.[59,60] It was shown that, as a rule, the hydrolysis proceeds in accordance with the S_N1 mechanism via the nitrilium ion (XIII):

$$R\overset{+}{C}{=}N{-}NR^1R^2 \longleftrightarrow RC{\equiv}\overset{+}{N}{-}NR^1R^2 \quad (XIII)$$

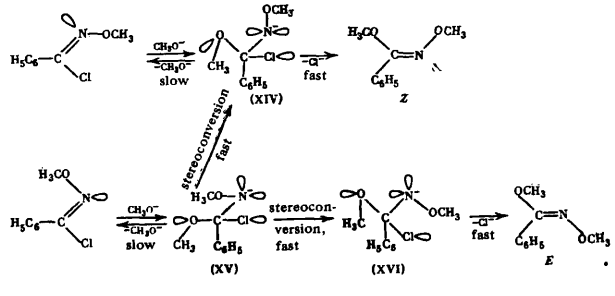
Electron-donating substituents at the imidoyl carbon atom (R) and the hydrazine nitrogen atom (R^1 and R^2) promote the formation of the nitrilium ion. Steric factors are also significant. Thus the rate of hydrolysis of *N*-arylhydrazonobromides with an alkyl group at the imidoyl carbon atom decreases with increase in the bulk of this group.[55] The hydrolysis of the hydrazonobromide group forming part of the composition of a heterocycle is difficult.[56]

(b) Reactions with Alcohols and Phenols

The familiar reaction involving the nucleophilic substitution of the halogen atoms in imidoyl halides and dihalides on treatment with alcohols or alkoxides, leading to the formation of the corresponding imidates, has been extended to new systems.[24,33,47,48,63-72] The interaction of *N*-(perfluoroisopropyl)acetimidoyl chloride with polyfluorinated alcohols has been carried out in the presence of trimethylamine,[66,72] while in the reactions of *N*-(pentafluorophenyl)carboimidoyl dichloride with alcohols and phenols, potassium carbonate has been used as the base.[64] It has been shown in relation to the interaction of *N*-arylbenzimidoyl chlorides and sodium phenoxides that aryl imidates can be obtained in satisfactory yields under the conditions of two-phase catalysis.[73,74] For a description of the reactions of *N*-trichloromethyl)carboimidoyle dichloride with alcohols and phenols, see Findeisen et al.[15]

The substitution of halogens by alkoxy- and aryloxy-groups has also been described for halogenoazines[51] and hydrazonohalides.[62,75-77] The reaction of *N*-arylhydrazonohalides with *o*-aminophenols leads to 1,4-benzoxazine derivatives.[78]

Not only a kinetic but also a stereochemical study has been made on the reactions involving alkoxide substitution at the N=C bond for benzohydroximoyl chlorides[71] and benzohydrazonochlorides,[75] although in many cases the configurational instability of the azomethine systems hinders such study. The reactions of the (*Z*)- and (*E*)-isomeric *O*-methylbenzohydroximoyl chlorides with sodium methoxide in solution in the 10% methanol–90% dimethyl sulphoxide (DMSO) mixture are characterised by the Hammett constant $\rho = 1.90$ and proceed with retention of configuration to the extent of ≥95% for the (*Z*)-isomer and 77–≥95% (depending on the substituents in the arene ring) for the (*E*)-isomer. The *E* → *Z* isomerisation of the initial chlorides does not then take place. The data obtained agree with a bimolecular mechanism for the addition–elimination reaction, in which the rate-determining stage is nucleophilic attack by the alkoxide ion on the initial chloride with formation of a tetrahedral intermediate:

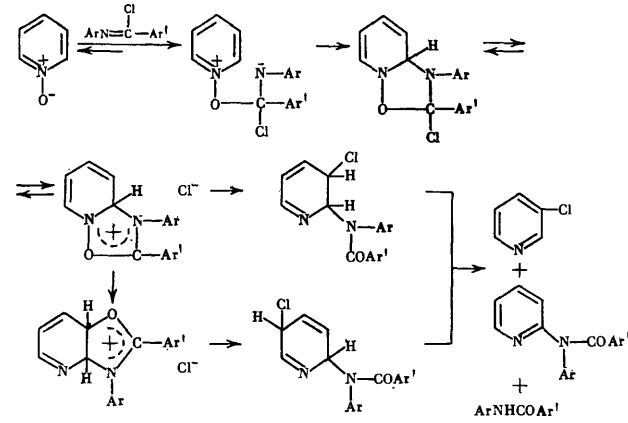


The stereochemistry and the relative rates of the reactions are interpreted in terms of the theory of the stereoelectronic control of the addition and elimination stages.[79] Accordingly, the loss of the chloride ion from the tetrahedral intermediate (XIV) is faster than the elimination of the methoxide ion with conversion into the initial compound or stereoconversion. The stereoconversion to the intermediates (XIV) and (XVI) proceeds more rapidly in the tetrahedral intermediate (XV).

A similar mechanism and stereochemistry have been established also for the reactions of *N*-arylbenzohydrazonohalides with the methoxide ion in methanol.[75]

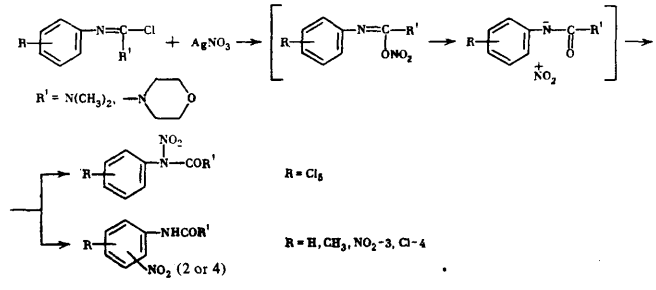
(c) Reactions with *N*-Oxides and Silver Nitrate

The *N*-oxides of nitrogen heterocycles interact with benzimidoyl chlorides to form heterocyclic derivatives containing 2-acylamino-groups, which readily hydrolyse to 2-amino-derivatives without being isolated.[80-83] Apart from the acylamination reaction, the chlorination of the heterocyclic ring and in certain cases the formation of hydroxy-derivatives are observed. In the presence of bases, the yield of the acylamination products increases. The reactions with pyridine *N*-oxides have been most fully investigated.[80,81] One of the reaction schemes is presented below:



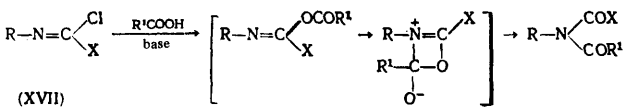
Ar = C_6H_5; Ar' = C_6H_5, $C_6H_4CH_3$-2, -3 and -4 etc.

Nucleophilic attack by the *N*-oxide oxygen on the electrophilic carbon atom of the imidoyl chloride and subsequent intramolecular addition of nitrogen in the 2-position in the pyridine ring leads to the intermediate, 1,2-dihydropyridine, which aromatises or undergoes a successive 1,5-sigmatropic shift and aromatisation. The primary products of the substitution of chlorine by the $-ONO_2$ group rearrange to nitroureas in the reaction of *N*-arylchloroformamidines with silver nitrate:[41]



(d) Reactions with Organic Acids

The reactions of salts of aromatic and aliphatic carxobylic acids or of the acids themselves with benzimidoyl chlorides or aryliminochloromethyl sulphides having the general formula (XVII) in the presence of bases take place via the nucleophilic substitution of the chlorine atom and the subsequent 1,3-migration of the acyl group from the oxygen to the nitrogen atom.[73,84] Satisfactory results have been obtained also under the conditions of two-phase catalysis:



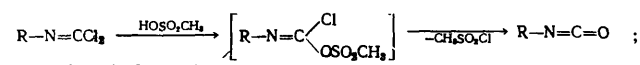
(XVII)

R=Ar, Alk; R'=Ar, Alk; X=C_6H_5, SC(Hal)$_3$

N-(Trichloromethyl)carboimidoyl dichloride reacts with aromatic, aliphatic, alicyclic, and heterocyclic carboxylic acids via the intermediate *N*-(chloroformyl) carboimidoyl dichloride in accordance with the scheme[15]

$$CCl_3{-}N{=}CCl_2 + R{-}COOH \rightarrow RCOCl + CO_2 + ClCN + HCl$$

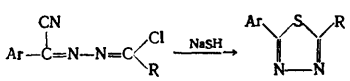
In the reactions involving aliphatic sulphonic acids, the final product is *N*-chloroformyl isocyanate. Isocyanates are obtained also in the reactions of carboimidoyl dichlorides with methanesulphonic acid:[17,85-87]



R=ClCH$_2$, CHCl$_2$, COCl

2. Reactions with *S*-Nucleophiles

The reactions of compounds containing halogenoimidoyl groups with aromatic and aliphatic thiols or their salts take place readily, leading to products of the substitution of the imidoyl halogen atom by a thio-group.[66,68,73,75,88-91] In many instances the reaction does not stop at the thioimidate formation stage and proceeds further, affording cyclisation products, 2,5-Disubstituted 1,3,4-thiadiazoles have been obtained in this way from, for example, 4-chloro-1-cyano-2,3-diazabuta-1,3-dienes:[2]



Ar=C_6H_5, $C_6H_4CH_3$-2, C_6H_4Cl-4; R=CH_3, C_6H_4Cl-2.

N-(Trifluoromethylthio)trifluoroacetimidoyl chloride, having two centres susceptible to nucleophilic attack (the imidoyl carbon atom and the sulphur atom), reacts with thiols as soft nucleophiles exclusively via the sulphenyl sulphur atom (the carbon atom is sensitive to attack by hard nucleophiles).[72]

Among other sulphur-containing reagents, phosphorus pentasulphide has been involved in the reaction, converting *N*-(dichloromethylthio)carboimidoyl dichloride into the corresponding isothiocyanate with a low yield.[93] The reactions of hydrazonohalides with various sulphur-containing reagents have been described by Shawali[9] and Hassaneen et al.[77]

3. Reactions with *N*-Nucleophiles

(a) Reactions with Amines

Primary and secondary amines. The reactions of compounds containing halogenoimidoyl groups with primary and secondary amines lead to the products of successive substitution of the halogen atoms at the imidoyl carbon atom by amino-groups. The compounds then formed are either entirely stable and can be isolated and characterised or they are unstable and undergo various conversions, in particular, carbodiimides or their tautomers (amidonitriles) and heterocyclic derivatives.

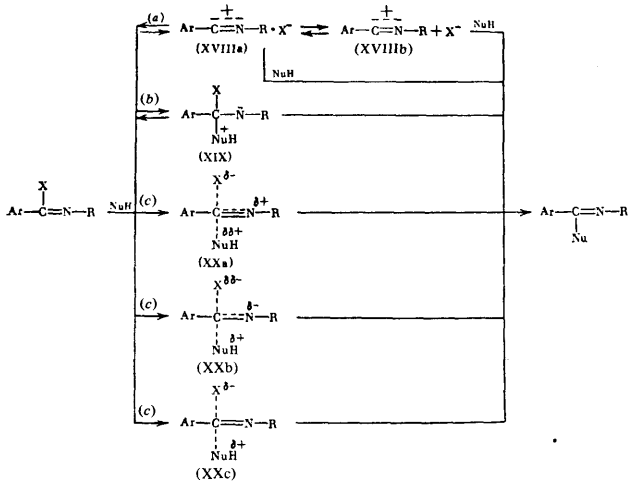
Stable substitution products have been isolated in the reactions of carboimidoyl dihalides,[41,45-97] imidoyl halides[37,48,65,72,95-109] hydrazonohalides,[59,77,91,110,111] and halogenoazines.[8] In certain cases trimethylsilyl derivatives of the amine were used for the reactions.[49,107]

It is noteworthy that, in the reactions of carboimidoyl dichlorides with aromatic amines, it is frequently not possible to obtain the products of the substitution of one chlorine atom and guanidines are formed.[17,46] They are present in the reaction mixture even when the degree of reaction of the initial dichloride is low.

Amidonitriles are formed in the reactions of *N*-(*p*-chlorophenyl)- and *N*-(pentachlorophenyl)-carboimidoyl dichlorides with ammonia.[3] Conversion into a carbodiimide has been noted in the reaction of 2,4,6,6-tetrachloro-1,1,1-trifluoro-2-phenyl-3,5-diazahexa-3,5-diene with t-butylamine. In the analogous reaction with isopropylamine or primary aromatic amines, derivatives of 1,2-dihydro-1,3,5-triazine were obtained.[112] Heterocyclic compounds have also been synthesised from carboimidoyl dichlorides and chlorides by reaction with ethylenediamine,[113] anilines,[15,108,114] and *o*-phenylenediamines[30,94,115-117] and also in the reactions of halogenoazines with amines.[8,35]

Kinetic data have been obtained for the formation of amidines in the reactions of diarylamidoyl halides with aliphatic[100,105,106] and aromatic[98,99] amines in non-aqueous solvents of different polarity and also in the reactions of isomeric *O*-methylbenzohydroximoyl halides with aliphatic amines.[109] Analysis of the influence of the nature of the substituents in the diarylimidoyl halide, the structure and basicity of the amine, the nature of the solvent, salt effects, and the effect of the leaving group and of the activation parameters supports bimolecular nucleophilic substitution at the imidoyl carbon atom with participation of the C=N bond. The substitution takes place via different pathways: (a) the nucleophilic elimination–addition mechanism characterised by negative values of the Hammett constant ρ in which the attack by the nucleophile on the nitrilium cation intermediate (XVIII) formed initially, which can exist either as the ion pair (XVIIIa) [the S_N2(IP) mechanism] or as the ion (XVIIIb) [the $S_N2(C^+)$ mechanism], is rate determining;† (b) the nucleophilic addition–elimination mechanism ($Ad_N - E$ or S_AN) involving the formation of the tetrahedral intermediate (XIX) and characterised by a positive value of ρ; (c) a concerted S_N2 mechanism which is differentiated in terms of the degree of involvement of the C=N bond (in terms of the relative contributions of the degree of dissociation of the C–Hal bond and the degree of formation of the C–Nu bond) into a dissociative bimolecular S_N2 mechanism with a transition state of type (XXa), where the degree of loosening of the C–Hal bond predominates over the degree of formation of the C–Nu bond (negative ρ), an associative mechanism where the opposite relative contributions obtain (the state (XXb), and a mechanism with a symmetrical transition state (XXc) with identical degrees of formation and loosening of the bond.

†The notation S_N2(IP) and $S_C2(C^+)$ represents respectively the ion-pair bimolecular nucleophilic substitution mechanism and the bimolecular nucleophilic subsitution mechanism with participation of the free ion and has been taken from Ta-Shma and Rapport.[105]



Pathways in which base, electrophilic, or bifunctional catalysis by an amine operates are also manifested, but their contribution to the overall process is small.

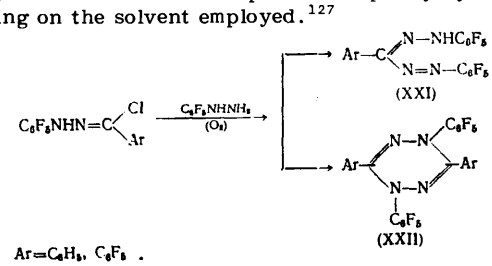
The $S_N2(IP)$ mechanism is preferable for the reactions of imidoyl halides having electron-donating substituents at the nitrogen atom with moderate nucleophiles and in solvents with a high solvating power, the version $S_N2(C^+)$ (pathway *a*) occurring for sterically strained nucleophiles. Pathway *b* is more characteristic of the reactions of substrates with electron-accepting substituents and strong nucleophiles. In intermediate cases, the diminution of the withdrawal of electron density from the azomethine linkage can be accompanied by the simultaneous operation of pathways *a* and *b*. Pathway *c* is less probable, but it cannot be rejected altogether especially since kinetic data do not always permit a clear-cut determination of the mechanism. For example, it is difficult to distinguish pathway *a* and pathway *c* with a transition state of type (XXa).[98]

The (*Z*)-isomers of *O*-methylhydroximoyl halides react with amines via an addition – elimination mechanism, while the (*E*)-isomers do not react.[109]

Tertiary amines are frequently used in the reactions of halogenoimidoyl compounds with nucleophiles in order to bind the HHal evolved or to generate ions (see below). However, instances of the addition of tertiary amines to halogenoimidoyl derivatives with formation of imidoylammonium salts are known. These reactions and their kinetics and mechanisms are described in detail elsewhere.[118–122]

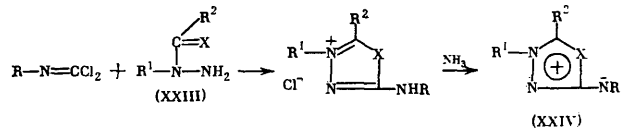
(b) The Reactions with Hydrazines and Their Derivatives

Hydrazines and their derivatives react with compounds containing halogenoimidoyl groups, forming stable primary products of the substitution of the halogen atom by the hydrazine residue[123–126] or the products of their further reactions. Thus mainly formazans (XXI) or tetrazines (XXII) are formed in the reactions of *N*-(pentafluorophenyl)-benzohydrazonochlorides with pentafluorophenylhydrazine depending on the solvent employed.[127]



Ar=C_6H_5, C_6F_5 .

Tetrazines are the products of the reaction of *N*-(arenesulphonyl)carboimidoyl dichloride with methylhydrazine in the presence of methyl orthobenzoate.[128] Substituted 1,2,4-triazoles or 2,5-diaryltetrazoles have been obtained by the reaction of *N*-(polychlorovinyl)imidoyl chlorides[108,114] and 1,3-dichloro-1-dimethylamino-4-fluoro-2-azabutadiene[129] or *N*-(benzenesulphonyl)benzohydrazonochlorides[130] respectively with arylhydrazines. The primary products of the reactions of *N*-(aryl)- or *N*-(alkyl)-carboimidoyl dichlorides with α-acyl- or α-thioacyl-hydrazines (XXIII) are converted into cyclic mesoionic compounds of type (XXIV) on treatment with ammonia:[131–134]



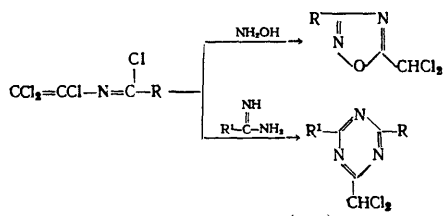
X = O, S

R^1 = CH_3; R^2 = C_6H_5; R = $C_6H_4CH_3$-4, C_6H_4Cl-4, CH_3 .

Mesoionic structures are also formed in the analogous reactions of 1,1-dibromo-2,3-diazadienes and *N*-aminobenzamidines.[125,134,135]

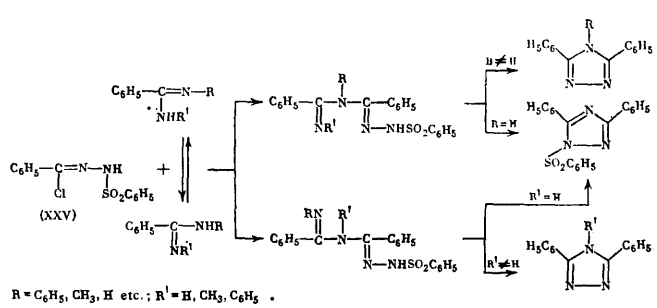
(c) Reactions with Hydroxylamine and Amidines

Carboimidoyl dichlorides and chlorides containing *N*-chloroalkenyl groups having α-chlorine atoms react with bifunctional nucleophiles, in particular, with hydroxylamine or amidines involving the substitution of an α-chlorine atom or the chlorine atom at the imidoyl carbon atom and affording various heterocyclic derivatives,[15,17,108,114] for example:



R=C_6H_5, C_6H_4Cl-4, $C_6H_4CH_3$-4, CCl_3 (etc.).

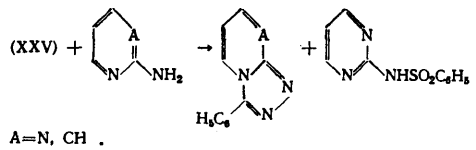
The reactions of *N*-(benzenesulphonyl)benzohydrazonochloride (XXV) with *N*-substituted amidines take place via a two-step mechanism involving the nucleophilic attack on compound (XXV) by two tautomeric forms of the amidine and subsequent cyclisation as a result of the nucleophilic attack by the amino-group on the iminocarbonyl carbon atom of the initial amidine in the intermediate compound. The final products are substituted 1,2,4-triazoles:[136]



R = C_6H_5, CH_3, H etc.; R^1 = H, CH_3, C_6H_5 .

2-Aminopyridine or 2-aminopyrimidine, which can be regarded as heterocyclic amidines, react analogously; the initial nucleophilic attack on the hydrazonochloride is by a ring nitrogen atom. This results in the formation of tri-

azolopyridines or triazolopyrimidines;



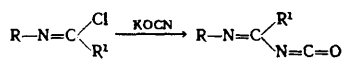
A=N, CH .

The reactions of other hydrazonohalides are similar.[137] Both linear and cyclic products are formed in the reactions of α-ketohydroximoyl chlorides with heterocyclic amidines.[138]

(d) Reactions with Azides and Cyanates

When compounds with a halogenoimidoyl group are acted upon by sodium azide, the halogen is replaced by the azido-group[57,139–143] and tetrazoles are formed.[51,84,139,144,145] The study of the kinetics of the reactions of isomeric acylbenzohydroximoyl chlorides with sodium azide in water showed that the reaction is bimolecular. When the (*Z*)-isomer is involved it takes place with retention of configuration, while in the case of the (*E*)-isomer it is ten times slower and the inversion of configuration is observed.[143]

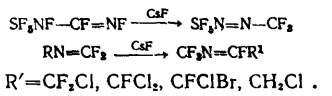
Open-chain imidoyl isocyanates, which have been little investigated, can be obtained by the reaction of imidoyl chlorides with potassium cyanates in the presence of crown-ether:[146]



R = iso-C_3H_7, C_6H_5 etc., R^1 = t-C_4H_9 .

4. Reactions with Halide Anions

The interaction of halogenoimidoyl compounds with the fluoride anion, whose source is as a rule caesium, potassium or sodium fluoride, has been most widely investigated. One of the reaction pathways involves the substitution of the imidoyl halogen atom by fluorine.[16,37,38,72,147–149] Under these conditions, other halogen atoms present in the molecule can also be substituted by fluorine[150,151] or these atoms alone are substituted if their mobility is higher than that of the halogen at the carbon atom of the N=C bond.[152] Another pathway in the reaction with alkali metal fluorides is isomerisation:[153,154]



R′=CF_2Cl, $CFCl_2$, CFClBr, CH_2Cl .

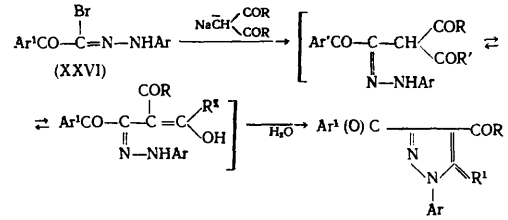
Finally, the addition of the fluoride anion to the N=C bond leads to the formation of *N*-anions, which can be inferred either from direct spectroscopic observations[155,156] and the isolation of stable salts[157] or from the reaction products. The anions can undergo intramolecular rearrangements and cyclisations[150,158,159] or they can participate in intermolecular reactions, functioning as active nucleophiles.[137,160] Dimerisation processes also belong to the class of intramolecular reactions.[159,161,162]

A study[159] of the interaction of the fluoride anion with perfluoro-2,5-diazahexa-2,4-diene established that the formation of a particular product is influenced by the source of the fluoride anion and the reaction conditions, which determine the formation of products resulting from kinetic or thermodynamic control.

The *N*-anion CF_3NF^-, formed by the reaction of $FN=CF_2$ with caesium, potassium, or mercury fluorides, behaves as an active nucleophile in reactions with the initial compound or its *N*-chloro-analogue and also with perfluorocarbonyl fluorides, giving rise to different products.[163,164] The less stable and nucleophilic *N*-anion CF_3NCl^-, formed by the reaction of $ClN=CF_2$ with potassium or caesium fluoride, is oxidised by chlorine to CF_3NCl_2.[164] The reactions of the *N*-anions derived from perfluoroazacyclohexene and perfluorocyclohexadienes have also been described.[155,156]

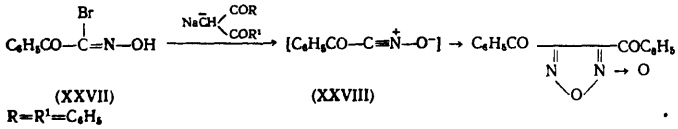
5. Reactions with *C*-Nucleophiles

The interaction of imidoyl chlorides or hydrazonohalides with KCN leads to the products of the substitution of the halogen by the CN group.[91,165,166] Carbanions generated from compounds with active methylene groups can also function as *C*-nucleophiles:[167]



R=R^1=CH_3, C_6H_5; Ar=C_6H_5; Ar^1=C_6H_5; $C_6H_4NO_2$-4 .

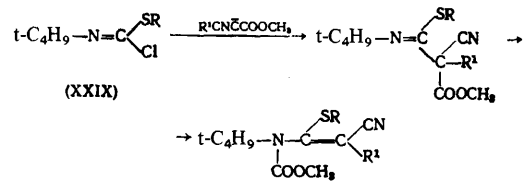
In contrast to this, in the reaction of hydroximoyl bromide (XXVII) with a carbanion, the latter acts only on the base, which promotes the formation of the intermediate nitrile oxide (XXVIII):[88]



R=R^1=C_6H_5

The difference in the behaviour of the two types of compounds, (XXVII) and (XXVI), can be attributed to the different acidities of the O–H and N–H bonds and to the ease of formation of the nitrile oxide from compound (XXVII) and the nitrile imine from compound (XXVI).

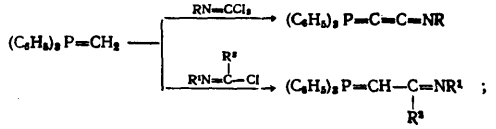
The interaction of chlorothioformimidates (XXIX) with carbanions derived from cyanomalonic esters leads to thioimidates which rearrange even at room temperature to the (*E*)- and (*Z*)-isomers of *N*-vinylcarbamates as a result of the 1,3-migration of the alkoxycarbonyl group:[168]



R=CH_3, C_6H_5; R^1=C_6H_5, $C_6H_4CH_3$-4 etc.

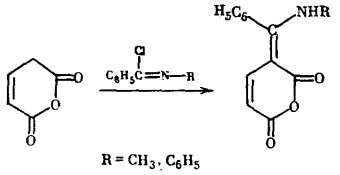
In the reaction of phenyl-lithium with *N*-(pentafluorothio)-chloroformamidine, the chlorine atom is substituted by the phenyl group.[47] Reactions with vinyl- and ethyl-magnesium bromides and also with aromatic and aliphatic magnesium bromide derivatives are described elsewhere.[42,89,171]

Carboimidoyl dichlorides react with methylenetriphenylphosphorane:[169,170]

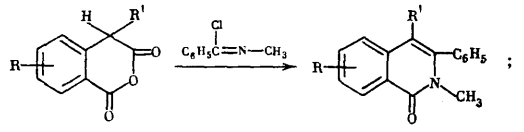


R=C_6H_5, CH_3, C_6H_{11} etc.; R^1=C_6H_5, $C_6H_4CH_3$-4;
R^2=C_6H_5, OCH_3, SCH_3 .

In reactions of glutaconic or homophthalic anhydrides with imidoyl chlorides, the initial nucleophilic attack on the imidoyl carbon ion is by the C(4) atom of the anhydride. The intermediate compounds of the aldol type are converted into the final products with and without the involvement of the anhydride component of the molecule:[172–174]



$R = CH_3, C_6H_5$



$R = H, OCH_3$ etc.; $R' = H, CH_3$.

6. Reactions with Other Nucleophiles

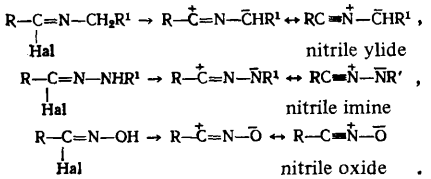
The reactions of imidoyl chlorides and hydrazonohalides with selenium compounds, leading to selenium heterocycles, have been described.[175,176] The mode of the reactions of imidoyl chlorides with di- and tri-alkyl phosphites[177,178] and also with phosphorus acid ester amides[179] depends unambiguously on the structure of the initial compounds and the reaction conditions. Imidoyl chlorides are converted into imines and amines on treatment with the $HFe(CO)_4^-$ anion in high yields,[180] while the reaction with the $C_6H_5COFe(CO)_4^-$ anion affords mesoionic 1,3-oxazol-5-ones.[181]

III. ELIMINATION REACTIONS

The elimination reactions of compounds with halogenoimidoyl groups have been fairly thoroughly investigated, particularly those which lead to highly reactive intermediate dipolar ions capable of interacting with various reagents to form new compound of many types. The wide scale use of halogenoimidoyl derivatives in organic synthesis, especially in the synthesis of heterocyclic compounds, is associated with precisely this feature.

1. The Formation of Ions and Their Reactions

When comounds with the halogenoimidoyl group are acted upon by strong bases, hydrogen halide is split off and dipolar ions of the following main types are formed:



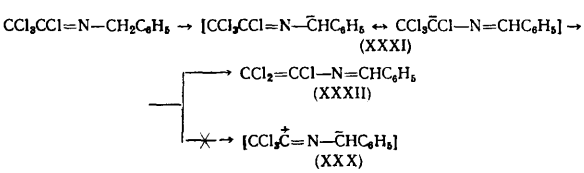
nitrile ylide

nitrile imine

nitrile oxide .

As a rule, these ions are formed only *in situ* and, depending on their structure and the reaction conditions, rapidly undergo intramolecular reactions or enter into intermolecular reactions with formation of dimers or the products of the reactions with other reagents present in the system.

In the course of development of early research into nitrile ylides, the mechanism of the tautomeric transformation of *N*-(4-nitrobenzyl)benzimidoyl chloride, *N*-(benzyl)-4-nitrobenzimidoyl chloride, and of the nitrile ylides formed from them on treatment with triethylamine has been studied in greater detail and confirmed experimentally.[182] Treatment of *N*-(benzyl)trichloroacetimidoyl chloride with triethylamine does not lead to the expected nitrile ylide (XXX), because the mesomeric carbanion (XXXI) formed initially is converted into *N*-(benzylidene)perchlorovinylamine (XXXII):[183]



(XXXI)

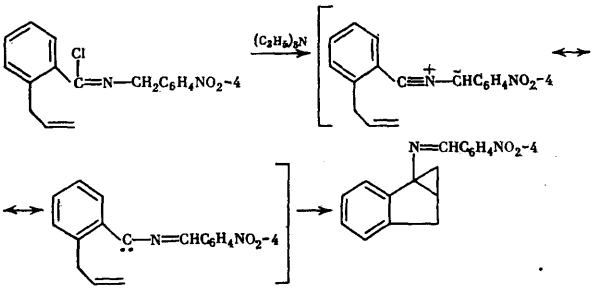
(XXXII)

(XXX)

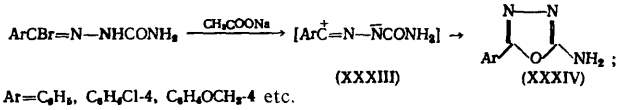
When the corresponding hydroximoyl chlorides were treated with triethylamine, acetonitrile oxide[184] and diphenylacetonitrile oxide[185] were obtained, the latter proving so stable that they could be isolated and characterised. Pentachlorobenzonitrile oxide is also extremely stable,[96] while pentafluorobenzonitrile oxide is unstable and readily dimerises. Silver nitrate has been used successfully to obtain the nitrile oxide from dichloroformaldoxime.[186] The attempt to obtain a nitrile imine from *N*-(benzenesulphonyl)benzohydrazonochloride was unsuccessful, which may be associated with the stability of the *N*-anion formed initially owing to the delocalisation of the negative charge on the electron-accepting benzenesulphonyl group.[136]

(a) Intramolecular Transformations of the Ions

The conversion of the nitrile ylide obtained from o-allyl-*N*-(*p*-nitrobenzyl)benzimidoyl chloride into a tricyclic compound as a result of the 1,1-cycloaddition of the carbene form of the nitrile ylide to the double bond may serve as an example of an intramolecular transformation:[187]



The intramolecular attack by the oxygen in the nitrile imine (XXXIII), which takes place as 1,5-dipolar addition, leads to the oxadiazole derivative (XXXIV):[188]



(XXXIII) (XXXIV)

$Ar = C_6H_5$, C_6H_4Cl-4, $C_6H_4OCH_3$-4 etc.

The nitronitrile imines formed as intermediates when the arylhydrazones of bromonitroformaldehyde are acted upon by sodium acetate in acetic acid isomerise to *N*-nitrosoaminoisocyanate, which is stable in the tautomeric cyclic mesoionic form of 3-aryl-1,2,3,4-oxatriazolate.[189,190]

The nitrile oxides formed from benzohydroximoyl chlorides on treatment with iron pentacarbonyl are deoxygenated further to nitriles.[191]

(b) Intermolecular Reactions of the Ions

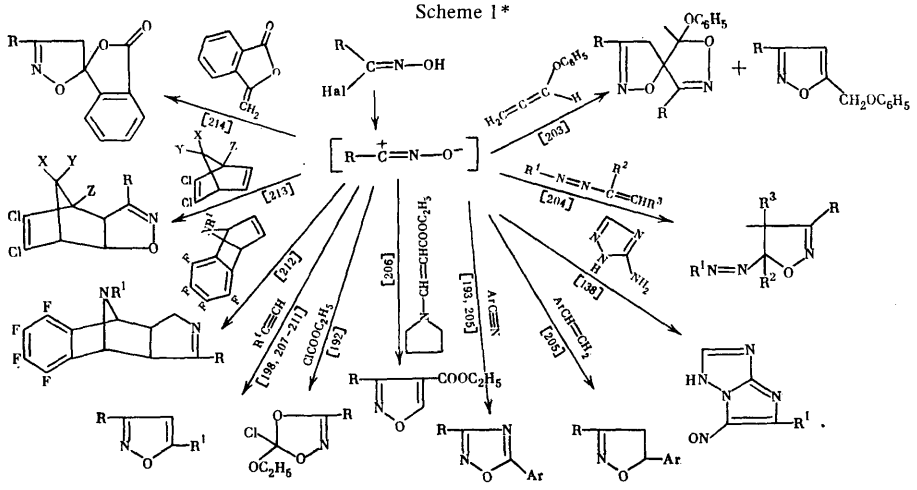
Dimerisation. The unstable nitrile oxides obtained from benzoylhydroximoyl halides[88,192] as well as acetonitrile oxide[184] and pentafluorobenzonitrile oxide[96] are converted into furoxan derivatives as a result of the 1,3-dipolar cycloaddition of one nitrile oxide molecule to the C≡N bond of another. Depending on the conditions under which trifluoroacetonitrile oxide is generated, its dimers are the corresponding dioxadiazine or furoxan.[193] Nitrile imines of the type $ArN^{-}-N=\overset{+}{C}-R$, where R = $COCH_3$, $COOC_2H_5$, or $COAr^1$, obtained from *N*-arylhydrazonohalides, dimerise to derivatives of 1,4-dihydro-1,2,4,5-tetrazine.[165,194]

Interaction with dipolarophiles and other reactions. The important and widely investigated reactions of the intermediate nitrile ylides, nitrile imines, and nitrile oxides involve their dipolar [3 + 2]cycloaddition interaction with various dipolarophiles occurring with the closure of a five-membered heterocycle ring and leading to the formation of a wide range of a wide variety of heterocyclic systems. At the present time the range of dipolarophiles used is extremely wide. The cycloaddition reactions proceed with participation of the C=C, C≡C, C=N, C≡N, C=O, C=S, and N=O bonds. Some examples of the 1,3-dipolar cycloaddition reactions of nitrile oxides are presented in Scheme 1.

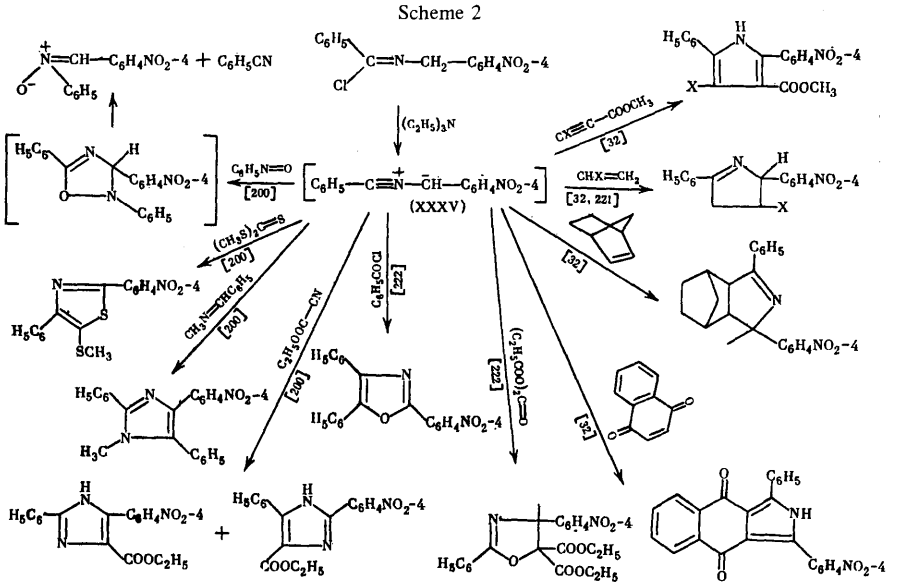
The reactions of nitrile oxides with other dipolarophiles have been described in a number of publications.[96,186,192,201,206,215–220] The 1,3-dipolar cycloaddition reactions of benzonitrile 4-nitrobenzylide are presented in Scheme 2. The reactions of the nitrile ylide (XXXV) with other dipolarophiles have been described by Huisgen and co-workers[32,222] and those of other nitrile ylides with dipolarophiles have been described by Padwa et al.[187] Scheme 3 presents the 1,3-dipolar cycloaddition reactions of nitrile imines. The reactions of nitrile imines with other dipolarophiles have been described in a series of publications.[194,199,202,212,228,230–232]

The mechanisms of these reactions have been described in a number of studies.[195–201] The most generally accepted point of view is that they take place via a concerted 1,3-di-

Scheme 1*



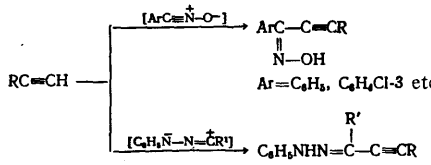
Scheme 2



Note. Numbers in square brackets denote references (Ed. of Translation).

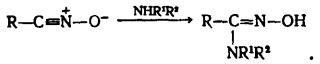
polar cycloaddition mechanism. The dipolarophile activity and mode of addition have been considered within the framework of the molecular orbital theory. The regioselectivity of the reactions is attributed to the ambident nucleophilic character of the 1,3-dipoles.

Nitrile imines and nitrile oxides are capable of entering not only into 1,3-dipolar cycloaddition but also into two-step 1,3-addition reactions with dienophiles, leading to acyclic products. For example, the reaction with acetylenes involves both processes and the second one leads respectively to acetylenic oximes or hydrazones:[195,198,202]

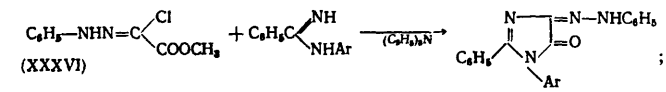


$R=C_6H_5$, $CH_2OC_6H_5$, $COOCH_3$; $R^1=CF_3$.

The reaction of nitrile imines and nitrile oxides with nucleophiles of different types (*N*-, *O*-, *S*-, and *C*-, and halogeno-nucleophiles) have also been investigated. The greatest number of publications refer to the reactions with *N*-nucleophiles. Primary and seconary amines react with nitrile oxides, affording amidoximes:[193,233,234]



Nitrogen-containing heterocyclic amino-derivatives are alkylated by nitrile imines at the most basic NH group of the ring and, if such a group is absent, at the NH_2 group.[226-228] Apart from the main product of cycloaddition to the C=N bond, 5-imidazolinones have been isolated in the reactions of the hydrazonochloride (XXXVI) with *N*-arylbenzamidines. Their formation is due to nucleophilic attack by the more basic amidine nitrogen atom (NHAr) of the electrophilic centre of the 1,3-dipole with subsequent ring closure involving a prototropic shift:[225]

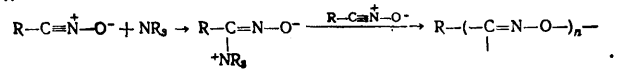


(XXXVI)

Ar=C_6H_5, $C_6H_4CH_3$-4 etc.

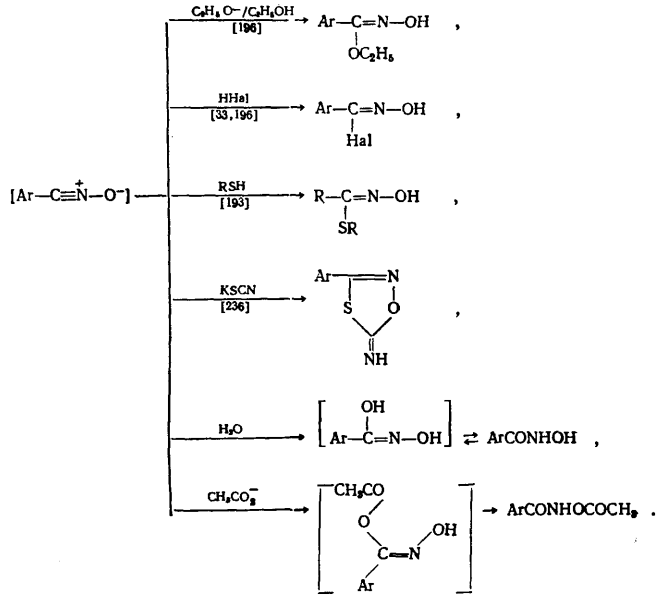
The reaction of nitrile imines with 1,1-diphenylhydrazine, carbohydrazides of the type $RCONHNH_2$, and the hydrazones of aromatic aldehydes and ketones involve the amino-group or proceed as 1,3-dipolar addition and lead to compounds of various types.[235]

Tertiary amines catalyse the polymerisation of nitrile oxides. They add to the nitrile oxides, giving rise to a zwitter-ion, which acts as a nucleophile on a second nitrile oxide molecule, etc.:[184,196]

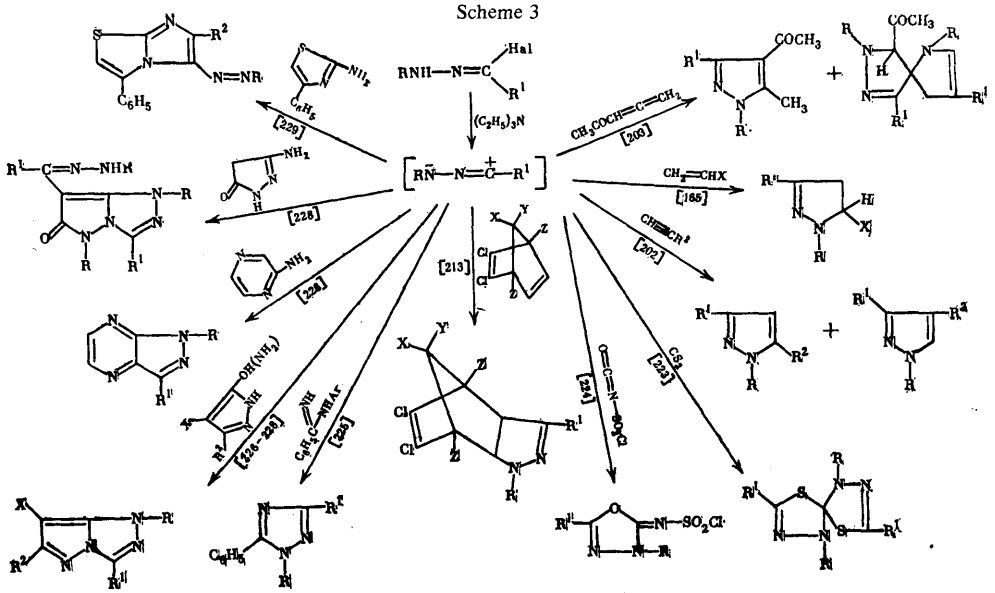


Hydroximoyl azides are formed as a result of the reaction of nitrile oxides with the azide ion.[196]

The interaction of nitrile oxides with *O*-, *S*-, *C*-, and halogeno-nucleophiles has been discussed in a number of studies.[33,193,196,197,233,236] "Open" oximes or the products of their further reactions are formed in these processes. Some of the reactions are presented below:



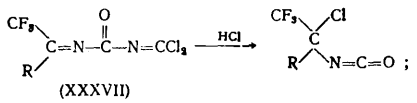
Scheme 3



2. Other Elimination Reactions

The familiar reaction involving the partial reduction of imidoyl chlorides to imines by treatment with tin dichloride has been used to convert a number of *N*-arylbenzimidoyl chlorides into aldehyde anils, from which aldehydes can be readily obtained in an acid medium.[237] In those cases where such a reductant cannot be applied, one can carry out the partial reduction under significantly milder conditions with the tris(t-butoxy)-derivatives of lithium aluminium hydride at a low temperature.[238] The reduction of imidoyl iodides with sodium tetrahydroborate leads to amines.[48] On treatment with magnesium in tetrahydrofuran (THF), *N*-(polyfluoroalkyl)- or *N*-(polyfluoroaryl)carboimidoyl dichlorides undergo reductive elimination of chlorine and the corresponding isocyanides are formed.[239]

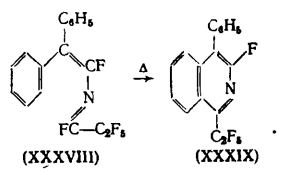
On heating with HCl, *NN'*-bisalkylideneureas of the type (XXXVII) split off chlorocyanogen with formation of α-chloroalkyl isocyanates:[240]



(XXXVII)

R=C_6H_5, C_6H_4Cl-4; $C_6H_4CF_3$-4 .

On thermolysis, imidoyl halides are converted into nitriles.[38,152,241] The high thermal stability of *N*-(pentafluorophenyl)carboimidoyl dichloride[161] and *N*-(pentafluorophenyl)chloroacetimidoyl chlorides[37] has been noted. Depending on the nature of the ring substituent, the thermolysis of benzohydroximoyl chlorides leads to nitriles, aryl isocyanates, or O-benzoylhydroximoyl chlorides.[242] *N*-(ω-bromopentyl)-benzimidoyl chloride undergoes fragmentation to ωω-dibromoalkane and benzonitrile on heating.[243] The azabutadiene (XXXVIII) splits off HF at 180–200 °C and is converted into the isoquinoline derivative (XXXIX):[244]



(XXXVIII) (XXXIX)

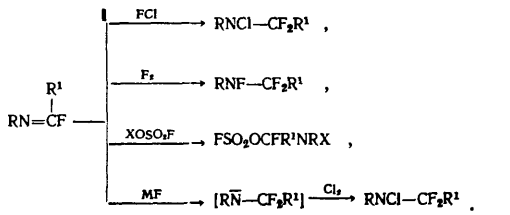
The thermolysis of compounds of the type $(RO_2C)_2N{=}N{-}CBrX$ (R = CH_3 or C_2H_5; X = Br or Cl) provides a new pathway to 2-halogen-1,3,4-oxadiazolin-5-ones which are difficult to obtain otherwise.[245]

Various chlorinated *SN*-heterocyclic systems are formed in the thermal dehalogenation reactions of polychlorinated imidoyl dichlorides and chlorides on treatment with sulphur.[246]

IV. ADDITION REACTIONS

1. The Action of Electrophiles and Radical Reagents

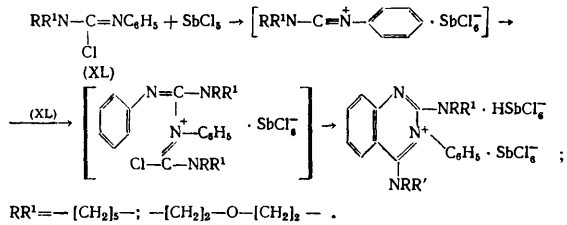
The reactions with electrophiles are less characteristic of compounds containing the halogenoimidoyl group than those with nucleophiles because of the electron-accepting properties of this group ($\sigma_m = 0.21$, $\sigma_p = 0.13$, $\sigma_I = 0.29$, $\sigma R = -0.08$[247]). However, such reactions are also known and in recent years their range has been appreciably extended. The interaction of halogenoimidoyl derivatives with the halogens,[248] including elemental fluorine,[249,250] chlorine monofluoride,[250–253] the highly electrophilic halogeno-derivatives of fluorosulphonic acid of the type $XOSO_2F$ (X = Cl, Br, or OSO_2F), the pseudohalogen $S_2O_6F_2$, and also moderately electrophilic halogeno-derivatives such as CF_3OCl and CF_3OF[164,148] has been investigated. These reactions involve the electrophilic or free radical addition of the reactants to the C=N bond. In many instances the reactions take place in the presence of alkali metal fluorides which promote the formation of the corresponding readily oxidisable *N*-anions:



The products of addition to the C=N bond are also formed in the oxidation of *N*-halogeno-, *N*-halogenoalkyl-, or *N*-pentafluorothio-imidoyl difluorides by trifluoromethyl hydroperoxide:[154,254,255]

$$RN{=}CF_2 + CF_3OOH \rightarrow CF_3OOCF_2{-}NHR$$

Lewis acids also enter into the addition reactions. This results in the formation of nitrilium salts,[243,256–259] which have been either isolated in a pure form or identified from the reaction products:

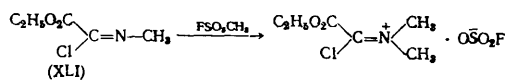


(XL)

RR^1=—$[CH_2]_5$—; —$[CH_2]_2$—O—$[CH_2]_2$— .

The interaction of SbF_3 with *N*-(chlorodifluoromethylthiosulphenyl)carboimidoyl dichloride is accompanied by the decomposition of the latter to chlorocyanogen and a disulphide.[260,261]

The imidoyl chloride (XLI) is alkylated by methyl fluorosulphonate to a reactive salt, whose formation has been detected from the ^1H NMR spectra and numerous reactions:[97]



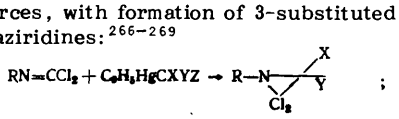
(XLI)

Treatment of imidoyl dichlorides with HF leads to the substitution of chlorine atoms by fluorine and addition to the C=N bond with formation of *N*-(trifluoromethyl)amino-derivatives.[157,262–264]

In the reaction of *N*-(t-butyl)carboimidoyl dichloride with bis(bistrifluoromethylamino-oxy)mercury, the final products resulted from the substitution of one or two chlorine atoms by the bistrifluoromethylamino-oxy-radical; the monosubstituted product can be converted into the disubstituted product by additional treatment with the mercury derivative.[264]

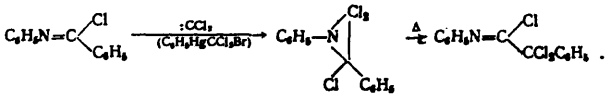
2. Cycloaddition

Aromatic and aliphatic carboimidoyl dichlorides enter into cycloaddition reactions with halogenocarbenes, obtained from mercury sources, with formation of 3-substituted 2,2-dichloro-1-phenylaziridines:[266–269]



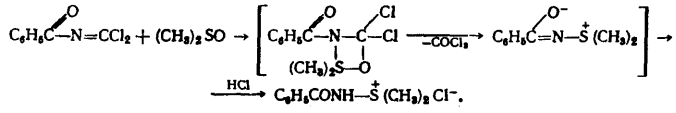
R=C_6H_5 Z=Cl or Br X=F; Y=$COOC_2H_5$
X=Y=Cl
X=F; Y=Cl .

The aziridine derivative of *N*-phenylbenzimidoyl chloride isomerises to the corresponding imidoyl chloride already during isolation:[266]



N-Phenyltrichloroacetimidoyl chloride does not react with dichlorocarbene.[266] Nor could *N*-pentafluorophenylcarboimidoyl dichloride be made to react with high-temperature sources of dichloro- and difluoro-carbenes.[161]

The cycloaddition to the N=C bond takes place in the reaction of *N*-benzoylcarboimidoyl dichloride with dimethyl sulphoxide; however, the cyclic adduct if unstable and decomposes under the reaction conditions with elimination of phosgene:[270]



During the preparation of the manuscript for publication, kinetic data were obtained for the arylaminolysis reactions of *N*-methane- and *N*-benzene-sulphonylbenzimidoyl chlorides in acetonitrile which are consistent respectively with the ion-pair and addition-elimination mechanisms.[271,272] The mechanism of the salt formation reactions of *N*-alkylbenzimidoyl chlorides with pyridine bases has been investigated.[273] It has been shown that the salt formation reaction of *N*-phenylcarboimidoyl dichloride and cyclic tertiary amines is accompanied by dealkylation with ring opening in the case of small rings.[274] The interaction of *N*-arylcarboimidoyl dichloride with cyclic secondary amines has been described.[275] The hydrolysis of chloroformamidines, the reactions of imidoyl chlorides and thioimidates with thiocyanates, and substitution of the chlorine atom in hydroximoyl chlorides on treatment with various nucleophiles have also been described.[275-279] The products of the reactions of perfluoroisopropylacetimidoyl chloride with *S*-, *P*-, and *N*-nucleophiles have been obtained in order to investigate the stereochemical isomerisation at the N=C bond.[280] 1,3-Prototropic migrations have been noted in the phosphorylation of imidoyl chlorides containing a hydrogen atom at the α-carbon atom. Bases also promote the migration of the chlorine atom.[281] In the reactions of *N*-phenylchloroformimidates, *N*-phenylthioformimidates, and *N*-phenylamidines with salts of phosphorus(IV) thio-acids, the 1,3-migration of the $X=P(OR)_2$ group from the sulphur atom to the nitrogen atom has been observed in the imidoyl phosphorothioates formed initially. Thiocarbamates, dithiocarbamates, or thioureas were then obtained as the products.[282] In contrast to other *P*-nucleophiles, dialkyl phosphites react with imidoyl chlorides at the oxygen atom, affording imidoyl phosphites.[283] The 2,2-dichloromalonamides having the general formula $(R_2N-CCl=N-CO)_2CCl_2$, which have been little investigated, react with monofunctional nucleophiles to give the products of the substitution of two chlorine atoms at the amidine carbon atoms. In the reactions with bifunctional reagents, cyclisation to heterocyclic spiro-compounds takes place.[284] The use of halogenoimidoyl derivatives as promising starting materials for the synthesis of a wide variety of heterocyclic compounds, formed directly in the reaction with nucleophiles or via further reactions of the products, has been demonstrated in studies on the reactions with azides,[285-287] with amines and hydrazines,[288-290] with carbanions,[291] and with copper and silver acetylides.[292] The synthesis of heterocyclic compounds with the aid of reactions involving the [2 + 4] cycloaddition of dicyclopentadiene to perfluoroimidoyl fluorides[293] and the reactions of the intermediate dipolar ions—either via their intramolecular cyclisations[294-296] or via their 1,3-dipolar cycloaddition to polarophiles[297-312]—has also been described. New data on the characteristics of the formation of dipolar ions and their structure and reactivity have likewise been published.[297,305-307] Problems concerning the formation, structure, and stereospecificity of the reactions of nitrilium ions have been considered.[307,308] Data concerning a convenient method of reduction of imidoyl chlorides to aldimines by treatment with hydrogen in the presence of palladium complexes and the reactions of these compounds with organotin compounds have been published.[309,310]

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General Principles and Characteristics of Cyclopalladation Reactions

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The factors influencing the ease and mode of the reactions involving the direct intramolecular cyclopalladation of organic ligands at sp^2- and sp^3-carbon atoms are analysed and the principal requirements which must be met by the structure of the ligand, the characteristic features of the coordination intermediates, and the experimental reaction conditions are considered. The bibliography includes 232 references.

CONTENTS

I. Introduction 250
II. Principal requirements for the ligand structure 250
III. Structural characteristics of the coordination intermediates 257
IV. Electronic effects in cyclopalladation reactions 260
V. Experimental conditions in the direct cyclopalladation reactions 261

I. INTRODUCTION

Cyclometallated complexes containing a comparatively reactive carbon–metal σ-bond stabilised by the additional coordination of the metal to a heterodonor atom of the same ligand are of great interest from several points of view. In the first place, cyclometallation processes are important as one of the ways of solving the most important current problems—that of the activation of the C–H bonds by transition metal compounds.[1,2] The study of the structures of stable cyclometallated complexes, which can be regarded as "frozen" intermediates in metal-catalysed chemical reactions, is a valuable source of information about the mechanisms of such catalytic processes.[3–5] The wide range of reactions with participation of cyclometallated compounds already known, which proceed with notable regio- and stereo-selectivity, leads to extensive possibilities for their synthetic application.[6–8] The cyclometallated compounds obtained in an optically active form can be used both for the synthesis of other chiral molecules,[9–12] and for the resolution of substrates with ligand properties,[13–18] and for the estimation of their optical purity.[19,20] Some of the cyclometallated complexes proved to be useful because of their liquid–crystal properties[21] or their high biochemical activity,[22,23] while others can be used to introduce heavy-atom and fluorescent labels into proteins and polypeptides.[24]

Since the synthesis of the first cycometallated complexes,[25] an enormous number of compounds of this class have been obtained (mono-, bi-, and tri-cyclic, mono-, di-, and trinuclear, and mono-, bis-, and tris-chelate) with metals having different electronic configurations (Pd, Pt, Ni, Rh, Ir, Ru, Re, Mn, Sn, etc.) and on the basis of a wide variety of ligands containing N, P, S, As, or O atoms as the heterodonors with M–C(sp^3) or M–C(sp^2) bonds involving an aliphatic, aromatic, olefinic, or acyl carbon atom; the complexes in which the M–C σ-bonds are stabilised by additional π-coordination can be formally also included in this class of compounds. A detailed discussion of each group of cyclometallated compounds is not of interest, especially since this has partly been done in review articles published previously,[26–42] which deal predominantly with data up to 1981. The analysis of the general principles of cyclometallation, which in the present review has been carried out in relation to the direct intramolecular cyclopalladation of ligands with heterodonor centres, is in our view of greater current interest.

Among all the known methods of synthesis of cyclopalladated complexes (CPC),[26] the direct palladation of a ligand coordinated beforehand via the heteroatom is the simplest and most convenient:



The terms "cyclopalladation"[43] or "*ortho*-palladation"—in the specific case of reactions involving the *ortho*-position in the aromatic ring of the ligand[44,45] were used to designate reactions of this type.

The ease and in many cases the very possibility of carrying out such processes depend on the structural features of the ligand and the intermediate coordination compounds and on the nature of the palladating agent and the reaction conditions. We have considered these factors in the present review.

II. PRINCIPAL REQUIREMENTS FOR THE STRUCTURE OF THE LIGAND

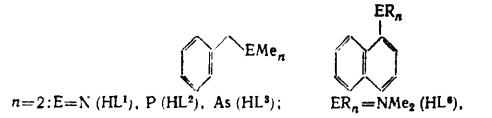
In order that the direct cyclopalladation of a particular ligand should be possible, its structure must satisfy a number of requirements concerning the nature of the heteroatom and its basicity, the possible size of the metallocycle, and the steric arrangement at the donor and metallated atoms within the chelate ring formed and outside it.

1. The Role of the Heteroatom

One of the necessary conditions for the successful palladation of a particular organic compound is the presence in the latter of a donor atom "directing" the reaction.[43,45–47] The formation of a transition metal–carbon σ-bond by direct metallation (without the preliminary coordination to the heteroatom) takes place in rare cases and is not characteristic of palladium. Intramolecular coordination to the heteroatom stabilises the C–Pd bond; the chelate effect is quite important in this connection. For example, the intramolecular cyclopalladation of azobenzene is 4×10^4 times faster than the intermolecular reaction of $PdCl_2$ with benzene;[48] the acceleration effect is associated with chelation via the azo-group, which converts the reaction from an intermolecular process to an entropically more favourable intramolecular process.

Preliminary coordination of the ligand to the transition metal atom is usually regarded as the first stage in the cyclometallation process.[45,48–51] It is therefore natural that the nature of the heteroatom should have a direct influence on the course of the reaction, which has in fact been confirmed by a whole series of facts.

The replacement of one heteroatom by another within the limits of the same general structure of the substrate can alter sharply its tendency to undergo cyclopalladation. For example, ligands of the types presented below form cyclopalladated complexes fairly readily (with $PdCl_4^{2-}$) only in the presence of a donor nitrogen atom—(HL^1) and (HL^6):[45,52–54]

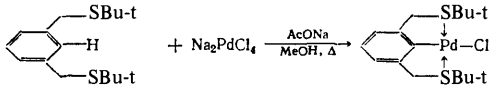


n=2:E=N (HL^1), P (HL^2), As (HL^3); n=1:E=O (HL^4), S (HL^5)

ER_n=NMe_2 (HL^6), PMe_2 (HL^7), SBu (HL^8)

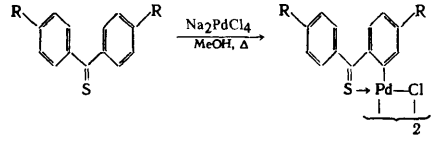
In the case of the dimethylphosphines (HL^2) and (HL^7) and arsine (HL^3), cyclopalladation does not occur and only coordination compounds of the type $[PdCl_2(HL)_2]$ are formed.[55–57] The introduction of oxygen, as in (HL^4), or sulphur, as in (HL^5) and (HL^8), as the donor atom also fails to stimulate metallation;[43,47,58] the thioether (HL^8) forms only a coordination compound. In their analysis of the failure of the attempts at the cyclopalladation of another *S*-donor ligand, namely benzyl phenyl sulphide, Takahashi et al.[59] concluded that the coordination of sulphur to palladium is so strong (compared with the analogous *N*-donor ligands) that it inhibits the further electrophilic substitution in the benzene ring under the influence of palladium(II). However, one should note that, when certain structural requirements and/or experimental conditions (see below) are observed, CPC based on phosphines[37] and thioethers[60,61] can be obtained.

In particular, the cyclopalladation process can be stimulated by doubling the number of thioether donor groups activating the *ortho*-position,[62,63] as happens, for example, in 1,3-di(*t*-butylthiomethyl)benzene:[63]



We may note that the monodentate analogue of this ligand is not metallated under the same conditions.

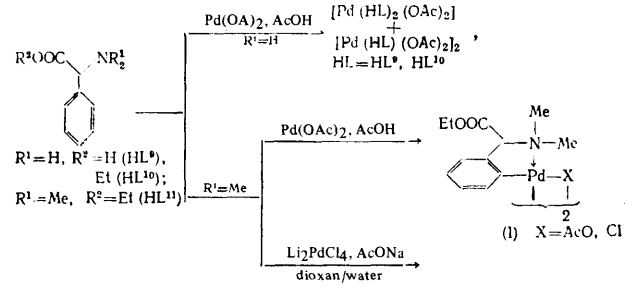
The degree of hybridisation of the donor atom has a significant influence on the ease of cyclopalladation. Thus, in contrast to the majority of thioethers (with the sulphur atom in the sp^3-hybrid state), which form only simple coordination compounds in the reactions with $PdCl_4^{2-}$ in methanol even on refluxing, thioketones[64–66] and thioamides[67–69] (containing a sulphur atom in the sp^2-hybrid state) undergo metallation comparatively readily under the same conditions. For example, CPC based on diaryl thioketones have been obtained:[66]



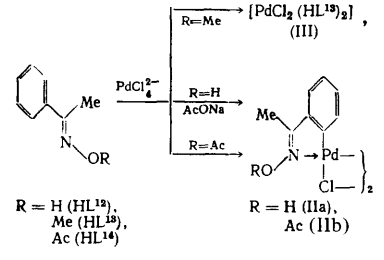
R=Me, MeO

The modification of the basicity of the initial ligand by altering the nature of the substituents at the heteroatom can also be significantly reflected in the rate and mode of the cyclopalladation reaction. For example, in view of the different reactivities of primary, secondary, and tertiary benzylamines, it has been suggested that the stronger *N*-coordination of the primary and secondary amines compared with the tertiary amine weakens the electrophilic properties of the metal to such an extent that this prevents the attack on the aromatic ring.[45]

Partly, for the same reason, it has not been possible to introduce into the *ortho*-palladation reaction either *C*-phenylglycine (HL^9) itself or its ethyl ester (HL^{10}), both containing a primary amino-group, while the *NN*-dimethyl derivative of the latter (HL^{11}) forms the CPC (I) both with palladium(II) acetate and with Li_2PdCl_4:[70,71]



This conclusion has also been confirmed by the comparative analysis of the reactivities of acetophenone oxime (HL^{12}), its *O*-methyl derivative (HL^{13}), and its *O*-acetyl derivative (HL^{14}) in the cyclopalladation reaction. The unsubstituted oxime (HL^{12}) undergoes *ortho*-palladation in the presence of sodium acetate with formation of compound (IIa), while its *O*-methyl analogue affords only the coordination compound (III) under these conditions:

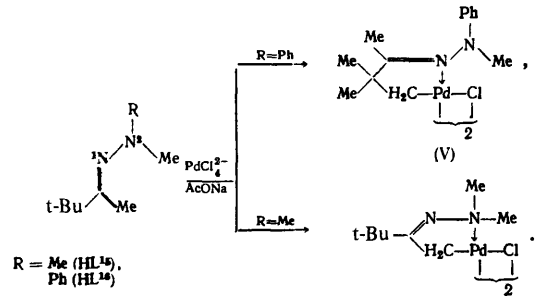


R = H (HL^{12}), Me (HL^{13}), Ac (HL^{14})

R = H (IIa), Ac (IIb)

The authors explained this by the fact that the stronger coordination of (HL^{13}) to palladium(II), induced by the presence of the electron-donating Me group, reduces the formal charge on Pd(2+), preventing the electrophilic attack by the latter on the aromatic ring. On the other hand, (HL^{14}), in which the coordinating capacity of the nitrogen atom is reduced owing to the introduction of the electron-accepting acetyl group, forms the *ortho*-palladised complex (IIb) even in the absence of a base.[72]

The study[73] of the causes of the regiospecificity of the cyclometallation of a number of hydrazones of aliphatic ketones provides a striking example of the influence of the comparative basicities of the heterodonor centres on the mode of cyclopalladation. In particular, it has been shown that the metallation of pinacolone dimethylhydrazone (HL^{15}) takes place at the methyl group attached to the azomethine fragment with coordination of the metal via the N(2) aminonitrogen atom [compound (IV)], which is unusual for hydrazones:

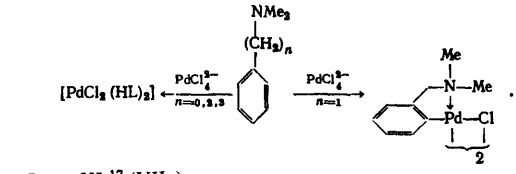


However, the introduction of the phenyl substituents at the N(2) atom, as in (HL^{16}), reduces its basicity (and hence its coordinating capacity), as a result of which the coordination of the metal via the azomethine N(1) atom becomes more favourable and, as a consequence of this type of preliminary coordination, the metallation of (HL^{16}) takes place at the methyl group in the t-Bu fragment [compound (V)].

Thus the presence of the heteroatom in the ligand is important for the stabilisation of the CPC formed, while the nature and the electron-donating properties of the heterocentre influence significantly both the reactivity of the metal and the mode of cyclopalladation.

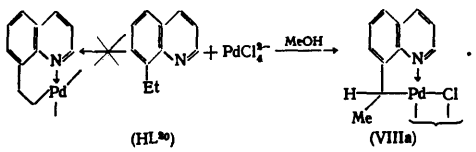
2. The Size of the Metallocycle

A clear-cut tendency towards the formation of a five-membered metallocycle is exhibited in the reactions involving the direct intramolecular cyclopalladation of the majority of organic ligands investigated. For example, in the series of amines of the type $Ph(CH_2)_nNMe_2$ (n = 0–3), only benzylamine (HL^1) is cyclopalladated, forming in this process the five-membered chelate ring (VIa);[45] the remaining ligands (HL^{17})–(HL^{19}) form only the simple coordination compounds (VIIIa–c):

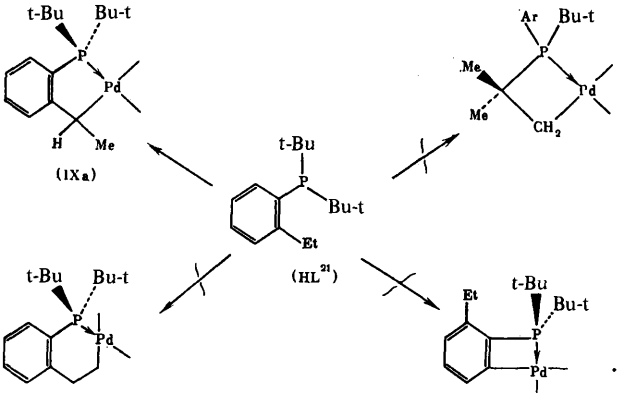


HL = HL^{17} (VIIa), HL^{18} (VIIb), HL^{19} (VIIc); n = 0 (HL^{17}), 1 (HL^1), 2 (HL^{18}), 3 (HL^{19})

In systems where there is a possibility of a choice between several modes of metallation, those leading to a five-membered metallocycle are as a rule realised. The dimeric CPC (VIIIa)[74–76] with a five-membered and not a six-membered metallocycle is formed in the palladation of 8-ethylquinoline (HL^{20}), despite the fact that a primary carbon atom is metallated more readily than a secondary carbon atom:[76]

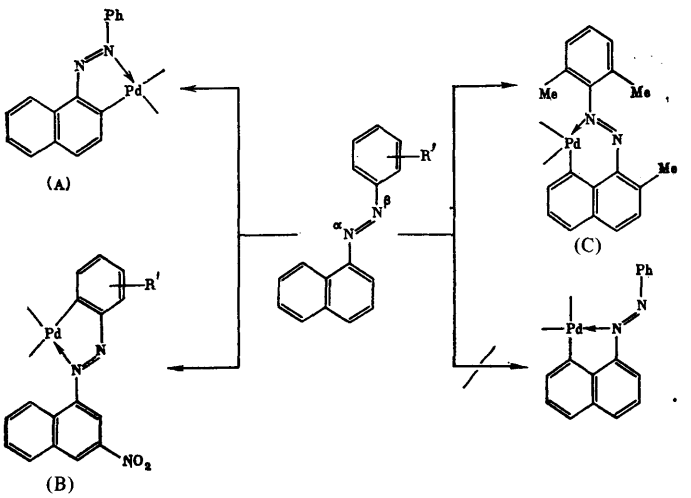


An analogous tendency has been observed also for *P*-donor ligands.[56,77,78] For example, several reaction pathways are possible for the cyclopalladation of the tertiary phosphine (HL^{21}): at the methyl group of the t-Bu fragment or in the free *ortho*-position in the benzene ring (with formation of four-membered metallocycles in both cases) and also the methyl or CH_2 group of the *ortho*-Et substituent (with formation of six- or five-membered rings respectively):



Despite the fact that the cyclopalladation at a secondary aliphatic carbon atom is more difficult than at a primary carbon atom (see below) or in an aromatic ring, the structure (IXa) with a five-membered metallocycle is produced in the experiment.[77]

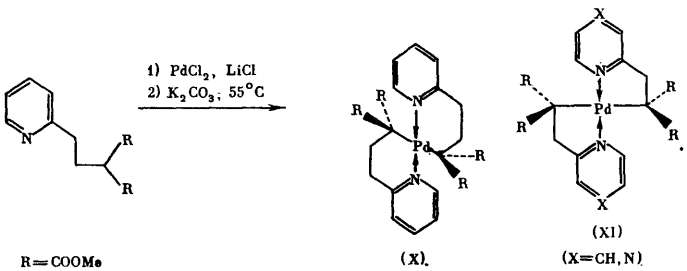
A marked tendency towards the formation of five-membered rings has been observed in a study of the behaviour of 1-arylazonaphthalenes under the conditions of the *ortho*-palladation reaction.[79–81] For ligands of this type, four versions of the closure of the metallocycle are possible, in principle, as a result of the presence of two donor nitrogen atoms and two aromatic rings suitable for metallation. In the absence of blocking groups, the reaction takes place preferentially via the C(2) atom of the naphthalene ring (A)[79] because of the greater accessibility of the N^{β} atom for preliminary coordination to the metal and the greater nucleophilicity of the naphthalene ring compared with the benzene ring; when strong electron-accepting substituents (the 3-NO_2 group) are introduced into the naphthalene ring and electron-donating substituents are introduced into the benzene ring, palladation at the benzene ring (B) becomes possible as a result of the change in the section involved in the preliminary coordination; a five-membered metallocycle is formed in both cases:



Only after the complete blocking by the methyl groups of all the sections suitable for the formation of five-membered rings (the 2′- and 6′-positions in the benzene ring and the 2-position in the naphthalene ring) is it possible to achieve

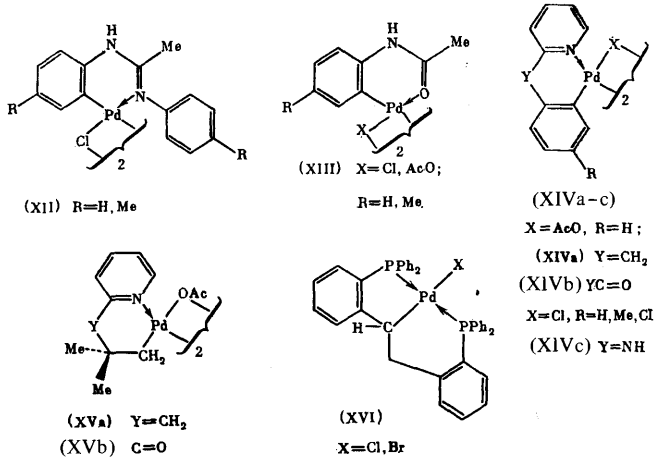
palladation in the *peri*-position in the naphthalene ring with formation of the six-membered metallocycle (C);[80] the involvement of the N^{β} atom in the structure (C) in coordination with the metal has been confirmed with the aid of ^{15}N NMR.[81]

It had been postulated earlier that the tendency by metals preferring the square-planar coordination to form five-membered metallocycles is associated with the necessity to maintain the ligand–metal–carbon intrachelate angle at a value near 90°.[82] The accumulated experimental data seem to confirm this "theory of five-membered rings". However, a recent comparison, based on X-ray diffraction analysis (XRA), of the structural features of complexes with five-membered[83,84] and six-membered[85] rings exhibiting the maximum structural similarity showed that the six-membered metallocycles can readily adjust to the requirement for a square planar environment of the metal; such complexes exhibit no unfavourable interactions and are obtained under the same conditions and with the same yields as their five-membered analogues.[85] The increase in the N–Pd–C intrachelate angle in structures of type (X) compared with (XI) is not accompanied by an appreciable loss of stability by the bis-chelates:[83-85]



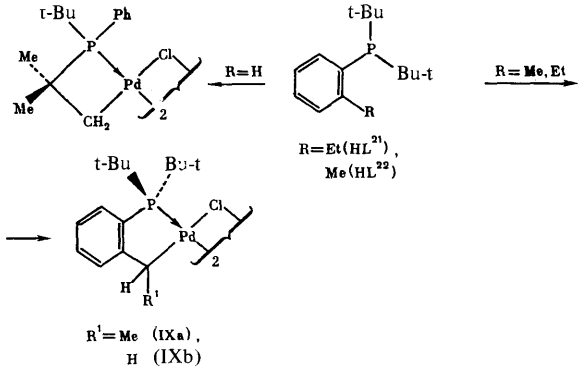
Fairly numerous CPC with six-membered metallocycles, based on different classes of ligands with N, O, and P donor atoms and obtained by the palladation at both sp^2- and sp^3-carbon centres, are known at the present time. Such complexes have been obtained from *N*-arylamidines (XII),[86] acid *N*-arylamides (XIII),[86-88] 2-benzylpyridine (XIVa),[89,90] 2-benzoylpyridine (XIVb),[90,91] 2-anilinopyridine (XIVc),[92] 2-neopentylpyridine (XVa),[93] 2-pivaloylpyridine (XVb),[94] and 2,2′-bis(diphenylphosphino)bibenzyl (XVI).[95,96]

It is noteworthy that in all the cases presented above the formation of six-membered metallocycles is enforced, since the ligand structures do not provide more favourable alternatives.

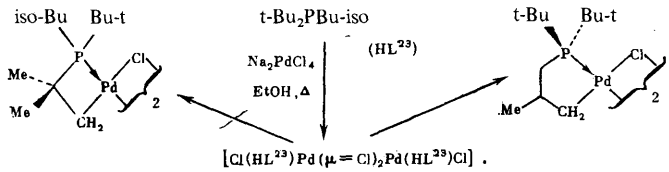


Four-membered metallocycles are also known—they are formed as a result of the direct intramolecular cyclopalladation of certain phosphines containing the t-butyl group.[97-100]

Nevertheless, here too the reaction pathway is enforced. When there is a possibility of the formation of a five-membered ring for ligands of this type, as happens, for example, in the case of (HL^{21})[77] or (HL^{22}),[78,101] the more favourable structure (IXa) or (IXb) respectively is in fact produced:



The cyclopalladation of di-t-butylisobutylphosphine (HL^{23}) also results in the formation of a five-membered and not a four-membered metallocycle:[102]



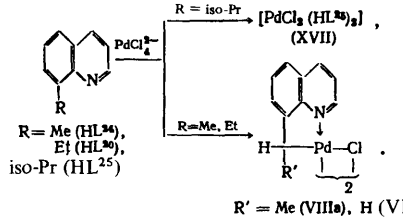
We may note that palladium(II) complexes with *N*-donor ligands, containing four-membered metallocycles, have not so far been isolated but the formation of such CPC has been postulated on the basis of spectroscopic data in a study of the mechanism of the amination of olefins in the presence of palladium compounds.[103]

Thus, despite the fact that the formation of five-membered metallocycles in CPC is in general preferred, there is no evidence, in principle, against the formation of either six-membered or four-membered metallocycles.

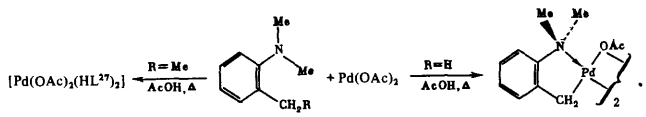
Analysis of the literature shows that the possibility of cyclopalladation and also the ease and mode of reaction are in many respects determined by the steric features of the initial substrate. Depending on their disposition in the molecule and the class of organic ligand, bulky substituents can neither promote or hinder the cyclopalladation reaction.

3. The State of the Palladated Carbon Atom

The problems of steric hindrance at the palladated carbon atom are especially acute in the direct metallation of aliphatic fragments. As was to be espected on the grounds of steric considerations, the ease of the cyclometallation of saturated carbon atoms decreases in the sequence primary > secondary > tertiary. For example, the palladation of 8-alkylquinolines takes place readily only when the 8-position contains a methyl group, as in (HL^{24}) and more slowly for the 8-ethyl derivative (HL^{20}); 8-isopropylquinoline (HL^{25}) forms only the coordination complex (XVII) under these conditions:[76,104]

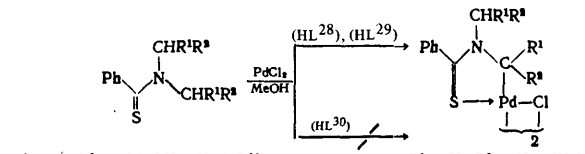


Whereas the metallation of a secondary carbon atom has been achieved in this system, albeit with difficulty, in the case of *o*-alkyl-*NN*-dimethylanilines, the CPC (XVIIIa) has been obtained only from the corresponding toluidine (HL[26]); palladation at the secondary carbon atom of the ethyl substituent in the ligand (HL[27]) has not been observed under any of the conditions used:[105]



R = H (HL[26]), Me (HL[27]) (XVIII)*a*

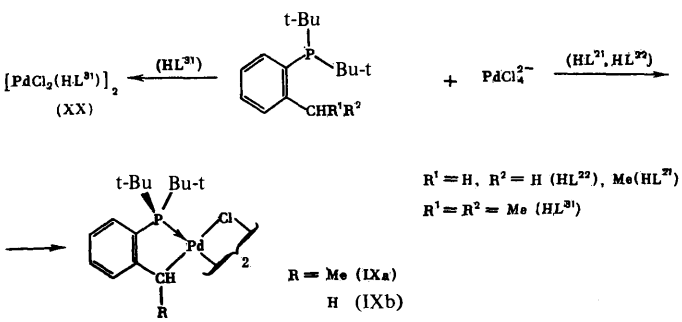
Analogous features have been observed in the series of S- and P-donor ligands. The study of the cyclopalladation of a series of *NN*-dialkylthiobenzamides demonstrated[67] a significantly greater reactivity of the *N*-Me group [the yield of the complex (XIXa) was 94%] compared with the *N*–Et group [the yield of compound (XIXb) was 13%], whereas the *N*-iso-Pr substituent in the ligand (HL[30]) could not be metallated at all:



$R^1 = H$, $R^2 = H$ (HL[28]), Me (HL[29]); $R^1 = R^2 = Me$ (HL[30])

$R^1 = H$, $R^2 = H$ (XIXa) Me (XIXb)

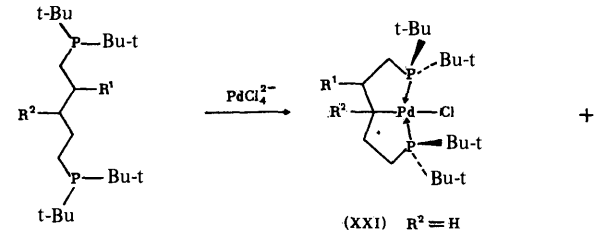
Palladation at a tertiary carbon atom in phosphines could not be achieved even in the presence of bulky substituents stimulating cyclometallation. Thus, whereas the cyclopalladation of di(t-butyl)-o-methylphenylphosphine (HL[22]) and di(t-butyl)-o-ethylphenylphosphine (HL[21]) takes place comparatively readily [structures (IXb) and (IXa)[77,78,101]], the ligand (HL[31]), containing the o-iso-Pr substituent, forms only the coordination complex (XX) under these conditions and the attempt to cyclopalladate it at elevated temperatures leads only to decomposition:[77]



$R^1 = H$, $R^2 = H$ (HL[22]), Me(HL[21])
$R^1 = R^2 = Me$ (HL[31])

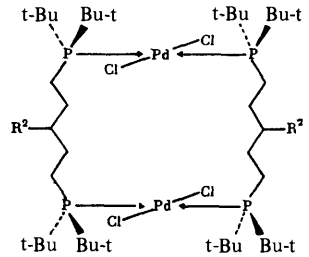
R = Me (IXa) H (IXb)

Similar features have been observed also in the formation of bicyclic CPC from a series of long-chain diphosphines. CPC could not be obtained from 1,5-bis(di-t-butylphosphino)-3-methylpentane (HL[32]) apparently precisely because of the difficulty of metallating a tertiary carbon atom; in the case of the unsubstituted derivative (HL[33]) and the 2-methyl derivative (HL[34]), where the metallation takes place at the methylene group, the CPC are formed, although in a low yield. The main product of the reaction with (HL[33]) and the only product in the case (HL[32]) is the dinuclear *trans*-complex (XXII) with bridging diphosphine ligands.[106–108]



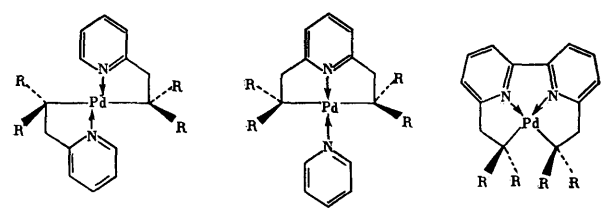
(XXI) $R^2 = H$

$R^1 = H$, $R^2 = Me$ (HL[32]), H (HL[33]);
$R^1 = Me$, $R^2 = H$ (HL[34])



(XXII) $R^2 = H$, Me

Cyclopalladation at a tertiary carbon atom takes place comparatively readily provided that the carbanionic centre thus produced is stabilised by electron-accepting substituents; this results in the formation of bis-chelate compounds (XXIII), bicyclic compounds (XXIV), or tricyclic compounds (XXV):[22,23,83,84]

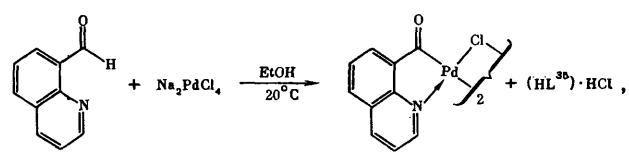


(XXIII) R = COOMe

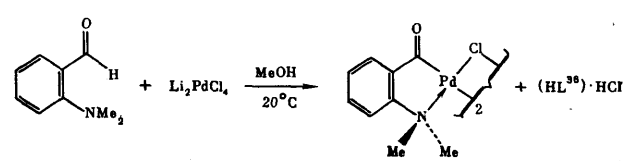
(XXIV) R = COMe, COOEt, CN

(XXV) R = COOMe, COOEt COOPr-iso

The ease with which the aldehyde functional group is palladised at the carbon atom is also noteworthy: acyl complexes are formed from aldehydes containing an additional donor group, in alcohol at room temperature without the introduction of an additional base:[109,110]



(HL[35]) (XXVI)

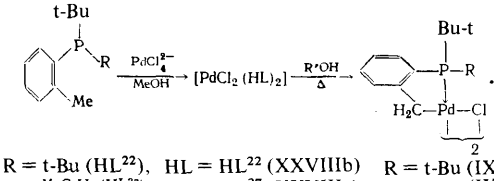


(HL[36]) (XXVII)

Thus a common feature is a decrease in the tendency towards cyclopalladation after the introduction of substituents at the carbon atom to be palladised; however, when such substituents are strongly electron-accepting, metallation is facilitated as a result of the increase in the acidity of the residual C–H bond and the resonance stabilisation of the carbanionic ligand.

4. Substituents at the Donor Heteroatom

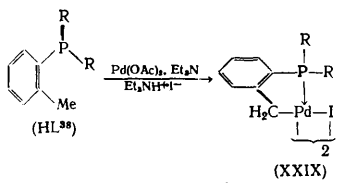
The steric hindrance at the donor heteroatom of the ligand can both promote and hinder its cyclopalladation. For tertiary phosphines, this process is greatly facilitated when bulky substituents are present at the phosphorus atom; for many of these compounds, an obligatory condition for successful cyclometallation is the presence of the t-butyl group.[56,77,78,97–101,111–113] This requirement refers to cyclopalladation both in the aromatic ring and in the aliphatic fragment. A far-reaching study of the cyclometallation of bulky phosphines has been carried out by Shaw and co-workers.[56,57,77,78,101,114–118] Comparison of the ease of the intramolecular palladation of the two phosphine ligands (HL^{22}) and (HL^{37}) in the coordination compounds (XXVIIIb, c) isolated beforehand showed that the rate of metallation of the ligand (HL^{22}), containing two t-butyl substituents at the phosphorus atom, is much higher than for the phosphine (HL^{37}), containing only one such bulky substituent:[78]



R = t-Bu (HL^{22}), o-MeC_6H_4 (HL^{37}); HL = HL^{22} (XXVIIIb), HL^{37} (XXVIIIc); R = t-Bu (IXb), o-MeC_6H_4 (IXc)

As an illustration of the lower tendency towards the cyclopalladation of arsines (compared with phosphines), we may note that ligands with an As donor atom, analogous to those described above, of the type $(t\text{-Bu})_n As(C_6H_4Me\text{-}o)_{3-n}$ (where $n = 1, 2$) do not undergo intramolecular metallation under the same conditions despite the introduction of even two bulky t-butyl substituents; heating of the *trans*-bis-complexes formed as intermediates with arsines coordinated as monodentate ligands via the heterodonor centre leads only to the segregation of zerovalent palladium.[119]

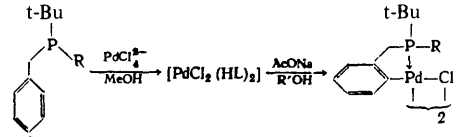
The cyclopalladation of tri(*o*-tolyl)phosphine (HL^{38}), which contains no t-butyl group, was considered for a long time to be impossible.[120] However, the formation of such CPC with (HL^{38}) (as a side product) was recently unexpectedly observed in the catalytic arylation reactions of conjugated polyenes, where the catalyst was the $Pd(OAc)_2$–(HL^{38})–Et_3N–$Et_3NH^+I^-$ system; the dimeric structure of the CPC (XXIX) with iodide bridges has been confirmed by X-ray diffraction analysis:[121]



(XXIX)

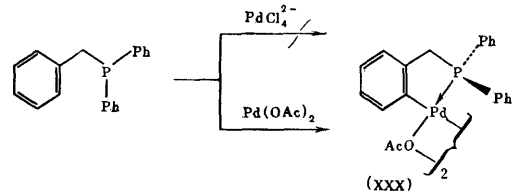
R = *o*-tolyl

An analogous stimulating effect of steric compression has been observed in the *ortho*-palladation of a series of benzylphosphines.[56] The rate of reaction decreases appreciably on passing from (HL^{39}) to (HL^{40}):



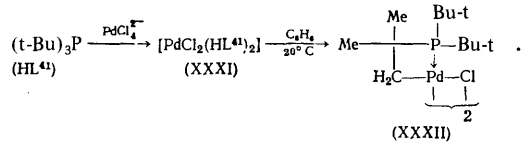
R = t-Bu (HL^{39}), $PhCH_2$ (HL^{40})

The *ortho*-palladation of phosphines not containing t-butyl substituents, for example, Me_2PCH_2Ph,[55] Ph_2PCH_2Ph, and $PhP(CH_2Ph)_2$,[122] does not occur at all under the same conditions. We may note that the *ortho*-palladated complex (XXX) based on Ph_2PCH_2Ph can be obtained only by using a more effective palladating agent—palladium(II) acetate:[112]



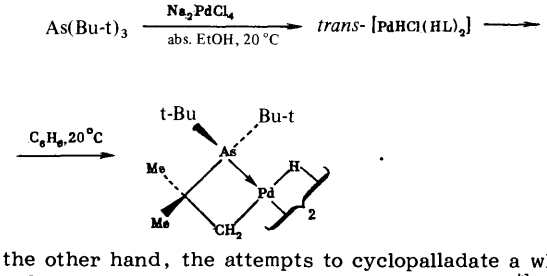
(XXX)

As was to be expected, in the case of tri(t-butyl)phosphine (HL^{41}), containing three bulky substituents, cyclopalladation takes place extremely readily: the bis-complex (XXXI) isolated beforehand is slowly converted into the cyclometallated compound (XXXII) even at room temperature in benzene,[98] the structure of the cyclometallated compound having been confirmed by X-ray diffraction analysis (XRA):[123]



(XXXII)

When three bulky t-butyl groups are introduced at the donor atom, intramolecular palladation of even an arsine ligand analogous to (HL^{41}) becomes possible, although in this case the reaction proceeds via a fundamentally different pathway with the intermediate formation of a stable hydride complex and its final product is the unusual hydrido-bridged dimeric cyclopalladated complex:[124]



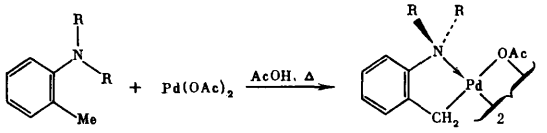
On the other hand, the attempts to cyclopalladate a whole series of less sterically hindered, compared with (HL^{41}), phosphines of the type of $R_2P(Bu\text{-}t)$ and $RP(Bu\text{-}t)_2$ (where R = Pr, Ph, or *p*-tolyl) were unsuccessful.[115] It follows from the calculation of the "cone angle" for such phosphines[98,115] that the steric compression in mixed alkylarylphosphines is much smaller than in (HL^{41}) and is insufficient to stimulate the formation of a four-membered metallocycle.

In his analysis of the causes of the effect of bulky substituents, which stimulate cyclometallation, Shaw[115] put forward several possible explanations. In the first place, we have the removal on metallation of unfavourable interactions between the phosphine and the adjoining ligand—for example, the halide in complexes of the type $[PdHal_2.(HL)_2]$. From the thermodynamic standpoint, the metallation

of bulky phosphines is accompanied by only a slight loss of rotational entropy, since rotation is strongly hindered even in ligands coordinated as monodentate species. If this is a kinetic effect, then one can assume that the free energy of activation for the metallation of sterically hindered phosphines is much lower than for the unhindered ligands as a consequence of entropic factors.

The "*gem*-dimethyl effect" is known in organic chemistry for small carbon rings ($n \leq 7$);[118] in the case of metallocycles involving larger atoms (phosphorus and metal) larger substituents are required for the stabilisation and easier formation of the rings, which results in the "*gem*-di-t-butyl effect".[118]

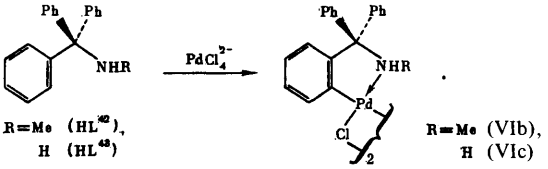
The characteristic features of the cyclopalladation of tertiary phosphines described above are not apparently characteristic of all types of ligands. Thus it is known[105] that the presence of bulky substituents at the nitrogen atom in *o*-alkylanilines hinders cyclopalladation: the replacement of *N*-methyl substituents by *N*-ethyl substituents decreases appareciably the yield of the CPC (XVIIIb) compared with (XVIIIa):



R=Me (XVIIIa) 70%
R=Et (XVIIIb) 8%

5. The Influence of Substituents in Other Fragments of the Ligand

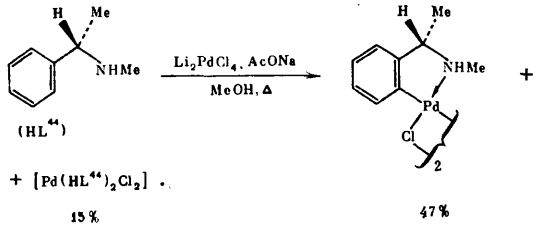
Steric effects due to the presence of bulky substituents at non-donor atoms of the ligand have a significant influence both on the rate of the cyclopalladation reaction and on its mode. Bulky substituents at the carbon atoms forming part of the metallocycle as a rule accelerate the reaction.[52,59,98,125,126] A striking illustration of this conclusion is provided by the results of a study of the cyclopalladation of benzylamines.[52] It is known that primary and secondary benzylamines do not form CPC under the conditions of the Cope–Friedrich reaction.[45] However, when two phenyl substituents were introduced in the α-position in the benzyl ligand, it was possible to obtain the CPC (VIb, c) from not only the secondary amine (HL^{42}) but also from the primary amine (HL^{43}):[52]



R=Me (HL^{42}), H (HL^{43})

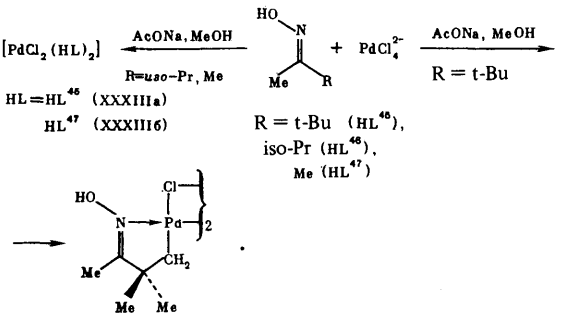
R=Me (VIb), H (VIc)

Later it was established[127,128] that a substituent in the α-position as small as the methyl group is quite sufficient for the successful cyclopalladation of secondary benzylamines:



It is noteworthy that the cyclopalladation of secondary amines is also facilitated with increase in the bulk of the substituent at the nitrogen atom: the *N*-isopropyl derivatives of α-methylbenzylamine and α-(2-naphthyl)ethylamine form CPC in 84 and 73% yields respectively.[127,128]

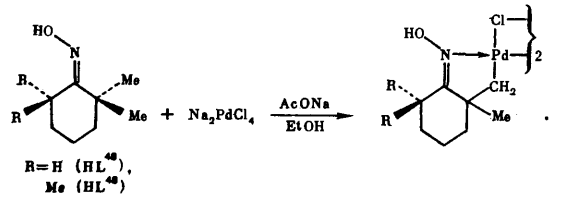
An obligatory condition in the cyclopalladation of oximes is the presence of the bulky t-butyl substituents at the keto-group,[125,126] for example, as in (HL^{45}); in its absence, as in (HL^{46}) and (HL^{47}), only the coordination compounds (XXIIIa, b) are formed:



HL=HL^{45} (XXXIIIa)
HL^{47} (XXXIII6)

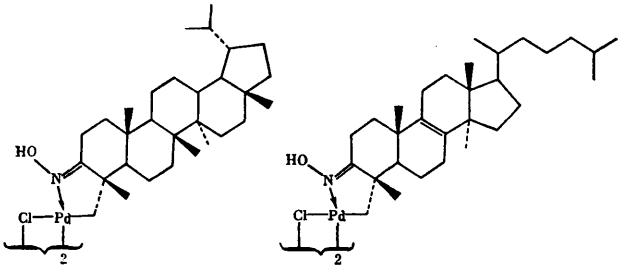
R = t-Bu (HL^{46}), iso-Pr (HL^{46}), Me (HL^{47})

Analogous features have been observed also for the oximes of cyclic ketones: (*E*)-2,2-dimethylcyclohexanone oxime (HL^{48}) and the strongly sterically hindered 2,2,6,6-tetramethylcyclohexanone oxime (HL^{49}) form CPC under standard conditions and in a high yield (~85%),[129] while the less sterically hindered 2-methylcyclohexanone oxime does not form cyclopalladation products:



R=H (HL^{48}), Me (HL^{49})

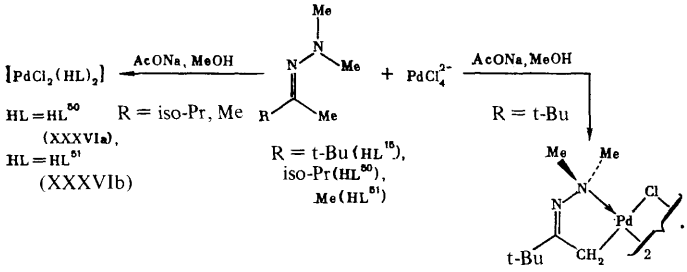
The possibility of the cyclopalladation of such fragments at the methyl group has been used successfully for the introduction of various functional groups into the non-activated methyl group in certain natural products, for example (*E*)-lupanone oxime[129] and lanost-8-en-3-one oxime[130] via the reactions of the corresponding CPC (XXXIV) and (XXXV):



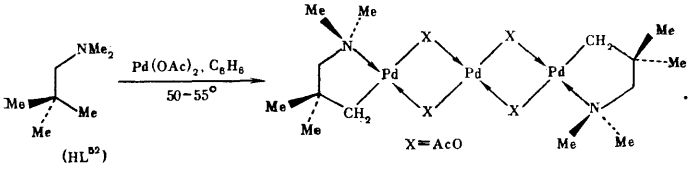
(XXXIV) (XXXV)

The presence of the t-butyl group at the carbonyl carbon atom is also necessary for the cyclopalladation of hydrazones,[125,126] but under these conditions the methyl group of the –N=C– fragment is metallated as a result of the preliminary coordination via the nitrogen atom of the amino-group and not via the imino-nitrogen atom of the ligand (HL^{15}). The less sterically hindered ligands (HL^{50}) and

(HL[51]) form only the coordination compounds (XXXVIa, b):

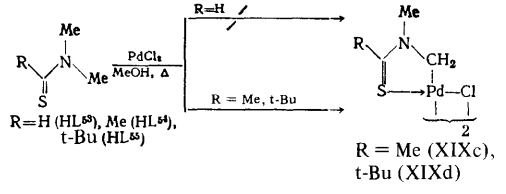


The successful cyclopalladation of dimethylneopentylamine (HL[52]) is apparently in fact caused by the presence in the ligand molecule of the bulky t-butyl fragment (and also by the possibility of the closure of the preferred five-membered metallo-cycle); it is of interest to note that the reaction product is in this instance an unusual trinuclear complex:[131]



The successful cyclopalladation of 2-neopentylpyridine[93] and 2-pivaloylpyridine[94] with formation of the CPC (XVa,b) is accounted for by analogous causes; here the stimulating influence of the steric hindrance overcomes the unfavourable closure of six-membered metallocycles (see Section 2).

Bulky groups at non-donor carbon atoms promote the cyclopalladation reaction also in the case of *S*-donor ligands—thioamides[67,68] and thioketones.[64] For example, whereas it was impossible to introduce *NN*-dimethylthioformamide (HL[53]) into this reaction under any conditions, the corresponding thioacetyl derivative (HL[54]) is converted into the dimer (XIXc) after refluxing with $PdCl_2$ in methanol for 10 h in 49% yield; the replacement of the methyl group in the acid residue by the t-butyl group, as in (HL[55]), makes it possible to obtain the CPC (XIXd) in 94% yield after 1 h:[67]



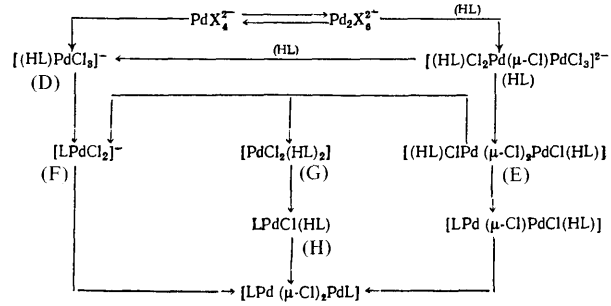
Thus the presence of bulky substituents at non-donor atoms in the ligands as a rule facilitates their cyclopalladation. The cause of this effect is analogous to the causes of the influence of the substituents at the donor phosphorus atoms in tertiary phosphines discussed previously (see above). Furthermore, the presence of bulky substituents in the ligand can lead to an enforced close approach by one of the protons to the metal atom within the framework of a simple coordination compound. Such interactions have been frequently confirmed by X-ray diffraction (see Section III).

III. STRUCTURAL CHARACTERISTICS OF THE COORDINATION INTERMEDIATES

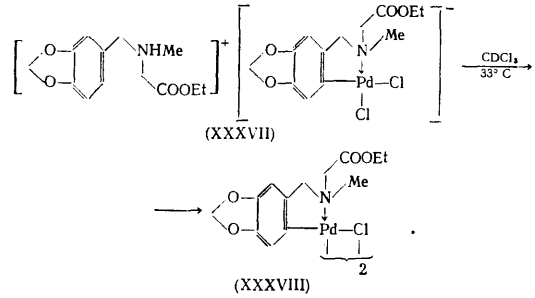
It has come to be assumed that the first stage in the cyclopalladation process is the coordination of the ligand to the transition metal atom. The alternative reaction mechanism—direct electrophilic metallation of the aromatic ring (analogously to the very familiar mercuration reaction) with subsequent chelation—is unlikely for metals in a low oxidation state to which palladium(II) belongs.[132]

The preliminary coordination of the initial ligand to the metal is acknowledged by the majority of investigators but the question of the specific structure of such coordination intermediates remains controversial. It apparently depends to a large extent both on the structure of the ligand and on the reaction conditions. For example, a study of the cyclopalladation of tertiary benzylamines[133] led to the postulation of several possible reaction pathways involving intermediates having different structures (Scheme 1):

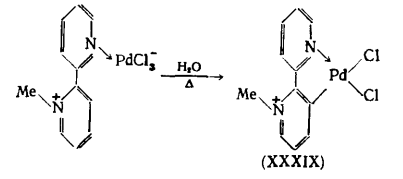
Scheme 1



Here X = Cl and (HL) and (L^-) are respectively the *NN*-dimethylaminobenzylamine ligands coordinated as a monodentate species and a 2*C*,*N*-chelated species. Some of the intermediate cyclopalladated and coordination compounds presented in Scheme 1 have been detected by spectroscopic methods or isolated in a pure state in the given and other ligand systems. For example, the mononuclear CPC (XXXVII) of type (F) has been isolated after treating the corresponding *NN*-disubstituted glycine ester with LiCl and $PdCl_2$ in methanol;[133] this compound is unstable and is converted already on dissolution in chloroform into the usual dimeric *ortho*-palladated complex (XXXVIII):

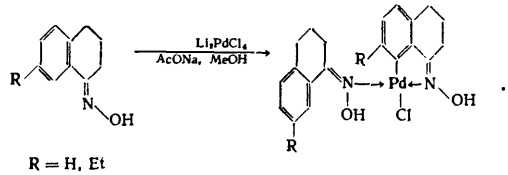


Stable mononuclear cyclopalladated compounds of type (F) are encountered comparatively rarely, but such a structure has been proposed, for example, for the product of the *ortho*-palladation of a cationic ligand—*N*-methyl-2,2′-bipyridylium (XXXIX):[134,135]



Complexes containing both a cyclopalladated ligand and a ligand bound as a monodentate species via the heteroatom [structure (H) in Scheme 1] have been isolated for certain reactant ratios in the *ortho*-palladation reactions of 1-tetralone

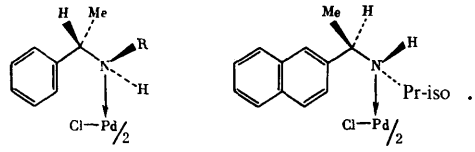
oximes:[136]



R = H, Et

Coordination compounds of type (G) belong to the class of the most typical stable intermediates—they have been isolated in a pure state in the cyclopalladation reactions of a wide variety of ligands: azobenzene,[50] hydrazones,[73] oximes,[72] aromatic primary amines,[137] sulphides,[60] thioamides,[69] tertiary phosphines,[78,98] and other ligands.[51,138] The isolation of coordination intermediates with tertiary benzylamines is hindered by the ready cyclometallation, but their 1:1 stoichiometry has been established with the aid of ^{1}H NMR even for the ratio $PdCl_4^{2-}$: $(HL^1) = 1:2$. Only one ligand is coordinated to the metal, while the other remains free.[139] It has been suggested that the first coordination intermediate is in this instance a dimeric coordination compound of type (E); the existence of the same type of intermediate has been suggested in the $Pd(OAc)_2$–(HL^1) system in $CDCl_3$.[133] However, kinetic and spectroscopic studies of the latter system in the presence of an excess of the ligand established[140] the rapid formation of a *trans*-bis-complex of type (G) (X = AcO), which is regarded as the initial state in the *ortho*-palladation reaction of (HL^1) in the given solvent.

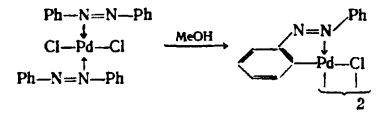
In the case of secondary benzylamines, whose tendency to undergo metallation is significantly reduced,[127,128] their coordination compounds of the *trans*-bis-type were isolated together with the cyclometallation products and were characterised by both spectroscopic and XRA methods:[141–143]



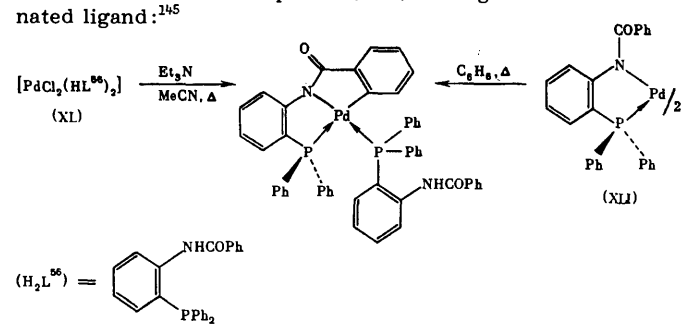
R = Me, iso-Pr

In the cyclopalladation of 1-tetralone oxime, the 1:1 stoichiometry of the intermediate was established by the ^{1}H NMR method and a dinuclear structure of type (E) and not an anionic structure of type (D) was attributed to it.[136] The formation of a similar dinuclear intermediate with the ligand coordinated as a monodentate species in the interaction of *trans*-$[PdCl_2(PhCN)_2]$ with the *N*-methyl-*N*-phenylhydrazone of pinacolene[73] even when a large excess of the ligand is used was attributed by the authors to the steric hindrance generated by the bulky substituents in the ligand. In other systems, there is a possibility of the formation of both mononuclear and dinuclear coordination intermediates depending on the reactant ratio. For example, complexes of types (E) and (G) have been isolated in the cyclopalladation reactions of di-t-butylisobutylphosphine[102] and pinacolone *NN*-dimethylhydrazone[73] for metal:ligand ratios of 1:1 and 1:2 respectively.

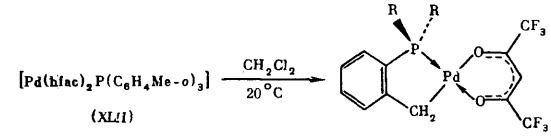
The most convincing evidence showing that the formation of coordination compounds with a monodentate ligand is one of the intermediate stages in the cyclopalladation process is provided by their ready conversion into CPC.[48,51,73,78,98,115,138,144], etc. Thus dichlorobis(azobenzene)palladium(II) can be readily converted into a cyclopalladated compound on heating[51] or by its simple dissolution in polar solvents (ethanol, methanol, aqueous dioxan):[48]



Several examples may be quoted to illustrate the wide variety of forms in which the first stage of the cyclopalladation process can take place (coordination via the heteroatom). Thus the *ortho*-palladation of the amidophosphine ligand (H^2L^{56}) can take place starting both with the traditional bis-complex comprising the ligand P-coordinated as a monodentate species, as in compound (XL), and with the bis-chelate compound (XLI) having an *NP*-coordinated ligand:[145]

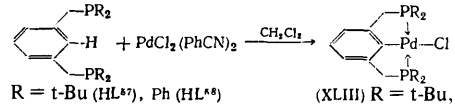


When palladium(II) bis(β-diketonates) are used to cyclopalladate bulky phosphines, pentacoordinated adducts of the type $Pd(hfac)_2(PR_3)$ (hfacH = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) are formed as intermediates, one of which, formed in the reaction with tri(*o*-tolyl)phosphine, has not only been isolated but has also been characterised by XRA.[146] This phosphine is cyclopalladated by simply allowing a solution of the adduct (XLII) in dichloromethane to stand at room temperature:[146]



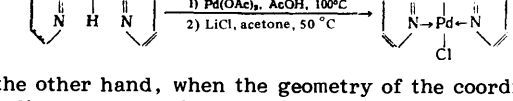
R = *o*-tolyl 47%

The ease and sometimes the very possibility of cyclopalladation depends significantly on the geometry of the complex with the ligand coordinated solely via the heteroatom. Thus it has been shown that complexes of the type *cis*-$[PdX_2(HL)]$ with the bidentate phosphines (HL^{57}) and (HL^{58}) are not converted into cyclometallated products, while the corresponding *trans*-complexes, in which the C–H bond has been activated in the vicinity of the metal atom, readily form CPC of type (XLIII):[147,148]



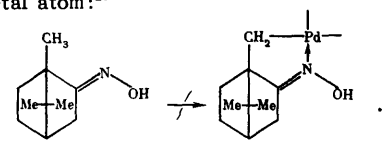
R = t-Bu (HL^{57}), Ph (HL^{58}) (XLIII) R = t-Bu, Ph

It may be that such activation of the central methylene group occurs also in the cyclopalladation of 1,3-di(2-pyridyl)-propane:[149]



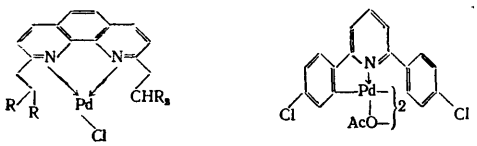
On the other hand, when the geometry of the coordination intermediate rules out for some reason a sufficiently close approach to the metal atom by the section to be metallated,

the metallation reaction becomes impossible. Thus, despite the formally close structural similarity of D-camphor oxime (HL^{59}) to the readily palladated pinacolone oxime,[125,126] all attempts to stimulate the conversion of its coordination complex *trans*-$[PdCl_2(HL^{59})_2]$ into the cyclopalladated derivative under various conditions were unsuccessful.[150] XRA of this complex established that the geometrical features of the molecule (especially the rigidity of the skeleton and the large Pd–N–C angles) prevent the methyl group from being close to the metal atom:[150]



(HL^{59}) (XLV)

The impossibility of the repeated metallation of substituted phenanthroline ligands in the monometallated complexes (XLIV), although their bipiridyl analogues do form doubly metallated derivatives fairly readily, has been explained by the increased rigidity of the central heteroaromatic fragment:[23]

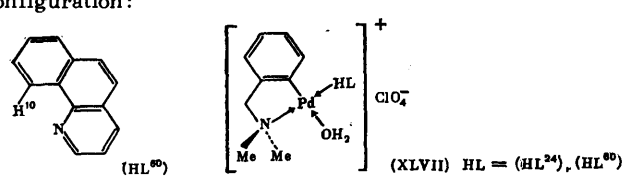


(XLIV) R = COOPr-iso (XLVI)

In their analysis of the causes of the failure of the attempt at the repeated palladation of 2,6-diarylpyridines, Selbin et al.[151] concluded on the basis of the XRA of the monopalladated dimer (XLVI) that, following the formation of the first strong, and therefore shortened, Pd–C σ-bond and also as a result of the increase in the Pd–C–C and C–C–C angles in the metallocycle with sp^2-carbon atoms, the metal "recedes" too far from the second aromatic ring and its metallation becomes impossible.

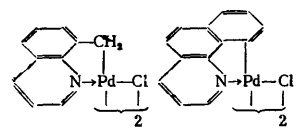
Analysis of the geometries of a number of coordination compounds on the basis of X-ray diffraction data demonstrated the occurrence in many palladium(II)[50,152] and also platinum(II)[153,154] complexes of specific intramolecular interactions which in fact make it possible to regard these complexes as possible intermediates in the cyclometallation of the corresponding ligands. A characteristic feature of the structure of the coordination compound of palladium(II) with azobenzene is an extremely close intramolecular contact of one of the chlorine atoms with the *ortho*-proton of the benzene ring and also fairly close contact (above and below the coordination plane) of the palladium atom with the *ortho*-protons of all four benzene rings of the ligands (two of these contacts are shortened).

Deeming and co-workers carried out a detailed study of the coordination chemistry of 8-alkylquinolines and benzo[*h*]-quinoline (HL^{60}) from the standpoint of the geometry of possible intermediates in the cyclopalladation reactions of these ligands.[86,104,155] In particular, they selected as test models the mononuclear *ortho*-palladated complexes of type (XLVII), in which the ligands investigated (HL^{24}) and (HL^{60}) are coordinated as monodentate species in the *trans-NN*-configuration:[155]



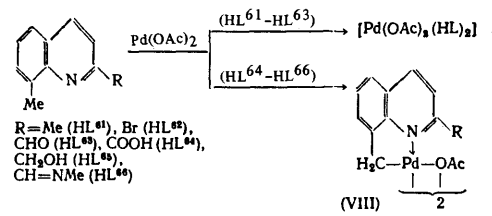
(HL^{60}) (XLVII) HL = (HL^{24}), (HL^{60})

It has been shown with the aid of ^1H NMR and also on the basis of the XRA of certain models that, in complexes of this type, one of the protons of the ligand coordinated as a monodentate species approaches the metal extremely closely: H(10) in the case of (HL^{60}) and the methyl group in the case of (HL^{24}). Such specific axial interactions in complexes with ligands coordinated as monodentate species are fully correlated in many cases with the pathway followed in the subsequent metallation: in the given instance, the ligands (HL^{24}) and (HL^{60}) are cyclopalladated in precisely the positions indicated above with formation of the dimers (VIIIa) and (XLVIII) respectively:[75,156]



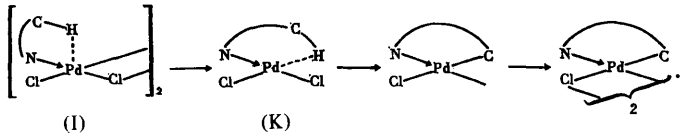
(VIIIa) (XLVIII)

However, despite the convincingly demonstrated reality of the axial interactions in the coordination compounds, it is still not clear for what position of the palladatable C–H bond relative to the coordination plane can its activation be the most effective. It has been suggested[155] that in square planar complexes of d^8 metals certain hydrogen atoms of the ligand are located above or below the coordination plane not as a result of bonding interactions but as a consequence of the endeavour to fill the unoccupied axial site, which reduces the repulsion. In particular, the much greater stability of the 7-methylquinoline complex compared with the analogous 8-methylquinoline compound clearly indicates the destabilising character of the enforced Pd...H–C interaction with the 8-methyl group of the ligand (HL^{20}). Further studies by these[76,86,104,156] and other[157] workers showed that the close axial approach by one of the protons of the ligand coordinated as a monodentate species does not always lead to the cyclometallation in this particular section. It is believed[104] that, under conditions where it behaves as an electrophile (which is in fact postulated in *ortho*-palladation reactions), the palladium atom should employ an unoccupied $d_{x^2-y^2}$ orbital, which requires cyclometallation in the coordination plane. The possibility of the activation of the C–H bond of the initial ligand in the coordination plane of the metal in cyclopalladation processes has been investigated by Deeming and co-workers,[76,104,156] who observed that the introduction of a substituent R in the 2-position in 8-methylquinoline can significantly modify the reactivity of the coordinated ligand. In the presence of groups such as Me, Br, and CHO in this position in the (HL^{61})–(HL^{63}) ligands, cyclopalladation does not take place, whereas for R=COOH, CH_2OH, or CH=NMe in the (HL^{64})–(HL^{66}) ligands, the latter are readily cyclopalladated at the 8-methyl group by palladium(II) acetate with formation of CPC of type (VIII):[158]



The authors suggest that the palladation of the 8-methyl group occurs only when the substituent R contains a [illegible] tive donor centre capable of participating in the [illegible] of the quinoline ligand (together with the quinolin[illegible] atom) and which thereby forces the 8-methyl group to approach the palladium atom in the coordination plane.

Spectroscopic analysis of the course of the *ortho*-palladation reactions of 1-tetralone oxime[136] and benzyldimethylamine[139] using low-temperature ^{1}H NMR spectra established that the axial and equatorial (within the coordination plane) orientations of the palladated C–H bond constitute two consecutive steps in the intramolecular metallation of these ligands:



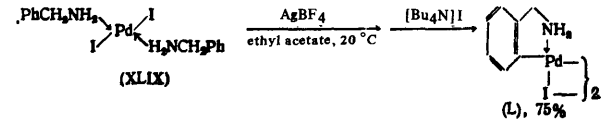
(I) (K)

In the case of tetralone oxime, it was possible to isolate from the aqueous medium at a reduced temperature (0 °C) the intermediate and most unstable (as regards cyclometallation) complex *cis*-$[PdCl_2(HL)].3H_2O$, whose spectroscopic characteristics indicate the location of the *ortho*-proton of the aromatic ring of the organic ligand in the coordination plane of the metal or close to it, which corresponds to a type (K) intermediate.[136]

The conversion of the intermediate (I) with an axial orientation of the C–H group into the intermediate (K) within the plane requires the liberation of one coordination site outside the metal. Pathways leading to the liberation of a coordination vacancy (in the given case apparently via the opening of the halide bridges) are not altogether clear, but there is no doubt about the importance of this stage in the cyclopalladation process.

Analysis of the kinetics of the cyclopalladation reactions of a series of substituted benzyldimethylamines by $Pd_2(OAc)_6^{2-}$ in acetic acid, led Sakodynskaya et al.[140] to the conclusion that the rate-limiting stage of the reaction is the formation of the coordination vacancy as a result of the dissociation of one of the acetate bridges in the adduct of the type $[(HL)(AcO)Pd(\mu\text{-}AcO)_2Pd(OAc)_2]^-$.

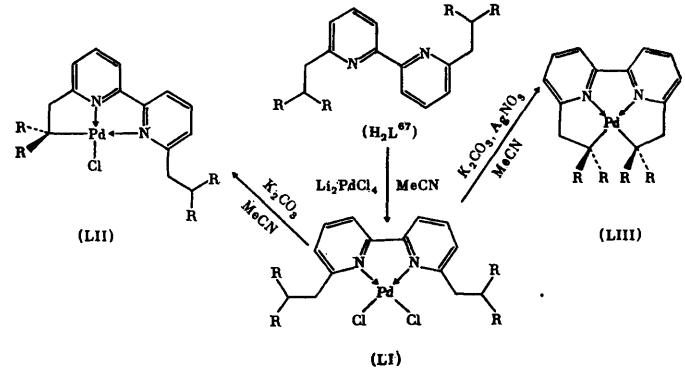
The most striking illustration of the importance of this stage in the cyclopalladation process is provided by the ready formation of the *ortho*-palladated dimer (L) with a high yield from the coordination complex (XLIX) when the latter is treated with two equivalents of $AgBF_4$, which effectively extracts iodide ions from the coordination sphere of the metal in the form of AgI:[159]



(XLIX) (L), 75%

This is particularly important because we are dealing with the palladation of the primary benzylamine which was for a long time believed to be impossible (see above). Naturally, the removal of halide ligands from the coordination sphere of the metal in the intermediate coordination compounds stimulates cyclometallation so effectively not only because of the liberation of the coordination vacancies but also as a result of the generation in this process of a stronger electrophile (Pd^{2+}), which is necessary for the second stage of the reaction—the electrophilic attack.

An analogous procedure has been used successfully to synthesise tricyclic CPC with two Pd–C(sp^3) σ-bonds in the *cis*-positions.[23] In the presence of sufficiently bulky substituents R in ligands of the type (H_2L^{67}), the coordination compounds (LI), isolated beforehand, are converted by bases only into monometallated derivatives (LII), while the introduction of $AgNO_3$ makes it possible to metallate both side chains with formation of compound (LIII):



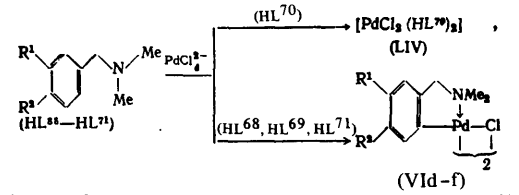
(LII) (LI) (LIII)

Compounds of type (LIII) with the *cis*(C)-geometry exhibit a high biochemical activity in relation to DNA,[160,161] while their *trans*(C)-analogues (LIII) have no biochemical activity.[22]

Although the studies discussed above do not provide a complete answer to the question of the mechanism of the activation of the C–H bond in the cyclopalladation process, they leave no doubt about the exceptional importance of the analysis of the structural features of the coordination compounds arising in the first stage of this process. The second stage of the process, the palladation proper, depends to a large extent on the electronic effects of the substituents in the ligand.

IV. ELECTRONIC EFFECTS IN CYCLOPALLADATION REACTIONS

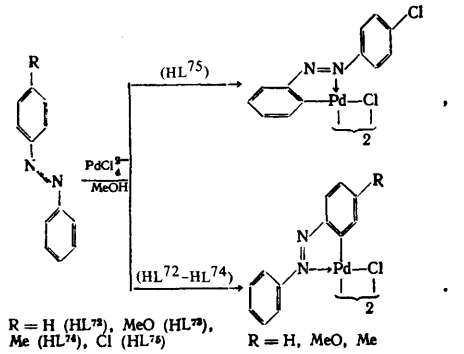
The electrophilic character of palladium(II) in the *ortho*-palladation reactions of various aromatic substrates is generally accepted and has been demonstrated experimentally. Electron-donating substituents (for example the methoxy- or methyl groups) greatly stimulate the *ortho*-palladation, while electron-accepting groups (for example, the nitro-group) partially or completely deactivate the aromatic ring. Such effects have been observed in the *ortho*-palladation reactions of benzylamines,[5,76,77,89] benzyl sulphides,[61] Schiff bases[162] and hydrazones,[163] and asymmetrically substituted azobenzenes[49,164] and 1-arylazonaphthalenes.[79,80] As an example, one may quote the results of a study of the behaviour of a number of benzyldimethylamines substituted in the aromatic ring.[45,165] While the ligands (HL^{68}) and (HL^{69}) with electron-donating substituents readily undergo *ortho*-palladation, the 3-nitro-derivative (HL^{70}) forms only the coordination compound (LIV). As an illustration of the marked acceleration of the reaction by several electron-donating substituents, one may recall the experimental conditions for the *ortho*-palladation of the ligand (HL^{71}): this benzylamine gives rise to the dimeric CPC (VIf) almost instantaneously at −78 °C in 95% yield:[165]



(VId-f)

R^1 = H, R^2 = MeO (HL^{68}, VId), Me (HL^{69}, VIe), NO_2 (HL^{70}); R^1 = MeO, R^2 = $MeSCH_2O$ (HL^{71}, VIf)

The study of the *ortho*-palladation of asymmetrically substituted azobenzenes,[49,164] 1-arylazonaphthalenes,[80] and dibenzyl sulphides[61] showed that both $PdCl_4^{2-}$ and $Pd(OAc)_2$ are electrophiles in these processes. The fact that palladation takes place preferentially in the aromatic ring of (HL^{73}) and (HL^{74}) having an electron-donating substituent and that of *p*-chloroazobenzene (HL^{75}) takes place exclusively in the unsubstituted phenyl group shows that the *ortho*-palladation occurs predominantly in that of the two aromatic rings which is more enriched in electrons:



R = H (HL^{72}), MeO (HL^{73}), Me (HL^{74}), Cl (HL^{75}) R = H, MeO, Me

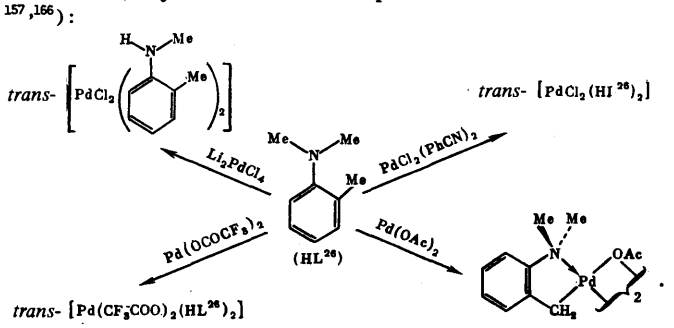
As was to be expected, the rate of *ortho*-palladation of compounds (HL^{72})–(HL^{74}) diminishes as a function of the nature of the substituent R in the sequence MeO > Me > H.[164]

V. EXPERIMENTAL CONDITIONS IN THE DIRECT CYCLOPALLADATION REACTIONS

Apart from the large number of structural factors influencing the ease and mode of cyclopalladation reactions, their success depends to a large extent also on the choice of conditions in the synthesis, namely on the nature of the palladating agent, the presence and nature of the base, the nature of the solvent, and the temperature and duration of the reaction.

1. Palladating Agents

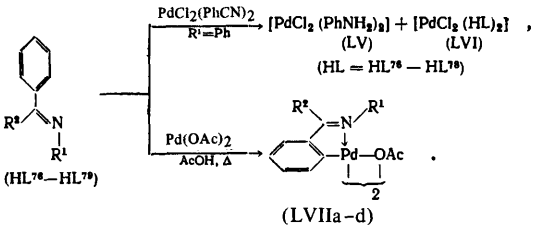
Both simple palladium(II) salts, namely $PdCl_2$ and $\{Pd(OAc)_2\}_3$, and coordination and chelate compounds of palladium(II), i.e. $M_2[PdCl_4]$ (M = Li, Na or K), $[PdCl_2(RCN)_2]$ (R = Ph or Me), $[Pd(acac)_2]$ (acacH = acetylacetone), and $[Pd(hfac)_2]$ are used as metallating agents in cyclopalladation reactions. The dependence of the reaction pathway on the nature of the metallating agents is clearly demonstrated by the reaction scheme for *NN*-dimethyl-*o*-toluidine (HL^{26}) under various conditions (only the main reaction products are indicated[105,157,166]):



trans- $[PdCl_2(HL^{26})_2]$ (HL^{26}) *trans*- $[Pd(CF_3COO)_2(HL^{26})_2]$

Historically the first method, proposed by Cope and Friedlich,[45] which is based on the interaction of the corresponding organic ligand with alkali metal tetrachloropalladate in the presence or absence of a base, is still used fairly widely for the synthesis of CPC.[44,45,52,165,167–169] Sometimes, the readily available palladium(II) coordination complex of benzonitrile *trans*-$[PdCl_2(PhCN)_2]$ is used for the cyclopalladation of organic compounds.[95,100,144,170] However, this method is not apparently distinguished by any advantages and does not always lead to the desired results.

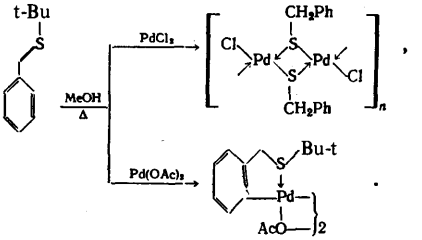
Palladium(II) acetate, which is regarded as the best electrophile in aromatic substitution reactions[176] and is a milder reagent for readily hydrolysable ligands, frequently proves to be a more effective palladating agent.[89,91,104,112,166,171–175] For example, it is known that Schiff bases, especially the aniline derivatives (HL^{76})–(HL^{78}), are extremely sensitive to hydrolysis, which is appreciably accelerated when they are coordinated to a metal.[172,177] Thus, in the attempts to orthopalladate the ligands (HL^{76}) and (HL^{77}) with the aid of $[PdCl_2(PhCN)_2]$ in methanol[172] or of the ligand (HL^{76}) with $PdCl_2$ in aqueous dioxan,[177] the coordination compound of aniline (LV), formed as a result of the hydrolysis of the Schiff bases, was isolated as the main reaction product together with only small amounts of the coordination compounds (LVI) of the initial azomethines. The *ortho*-palladated compounds (LVIIa–d), based on the corresponding Schiff bases, were obtained only when $\{Pd(OAc)_2\}_3$ was used as the metallating agent in glacial acetic acid:[172]



(LVIIa–d)

R^1 = Ph, R^2 = H (HL^{76}, LVIIa), Me (HL^{77}, LVIIb), Ph (HL^{78}, LVIIc); R^1 = Me, R^2 = H (HL^{79}, LVIId)

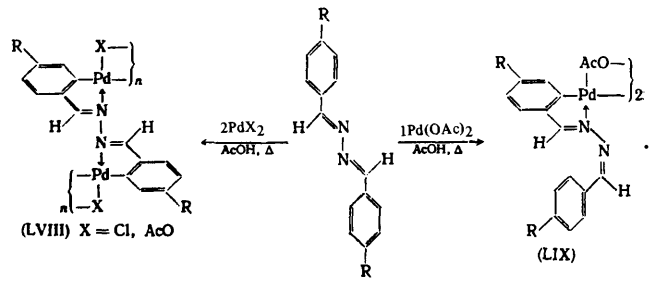
The *ortho*-palladation of benzyl t-butyl sulphide was achieved with the aid of palladium(II) acetate,[60] whilst all the attempts to cyclopalladate this ligand by treatment with Na_2PdCl_4 in alcohol (in the presence and absence of AcONa) or with $PdCl_2(PhCN)_2$ in dichloromethane or toluene were unsuccessful;[63] the use of $PdCl_2$ as the metallating agent leads to the dealkylation of the thioether ligand with formation of the polymeric complex $[\{Pd(\mu\text{-}Cl)(\mu\text{-}SCH_2Ph)\}_n]$:[60]



The successful *ortho*-palladation also of a series of less sterically hindered thioether ligands, namely benzyl izobutyl sulphide,[178] certain dibenzyl sulphides, and also dibenzyl sulphoxide,[61,179] with the aid of palladium(II) carboxylates as metallating agents is evidence for their high effectiveness.

By varying the palladating agent, it is possible to attain different degrees of metallation of ligands which provide several potential regions for this purpose. For example, in the reaction of benzylideneazines with $PdCl_2$, only the polymeric dicylcopalladised compounds (LVIII) are formed,[163] while in the reaction using $Pd(OAc)_2$ it is possible to isolate both the monometallated derivatives (LIX) and the dimetallate

derivatives (LVIII) depending on the conditions:[180,181]

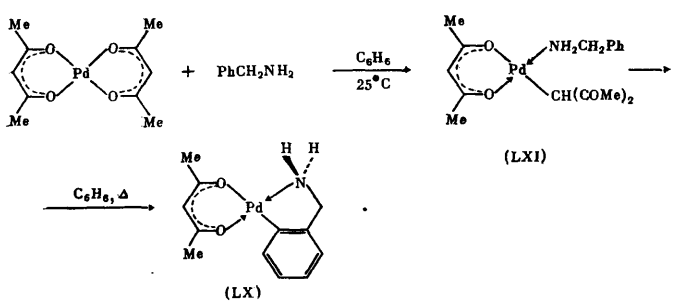


(LVIII) X = Cl, AcO (LIX)

The advantages of palladium(II) acetate as a palladating agent are especially evident in cyclometallation with participation of aliphatic fragments. For example, *NN*-dimethyl-*o*-toluidine (HL^{26}) is metallated by $Pd(OAc)_2$ with an almost quantitative yield, while under the conditions of the Cope–Friedrich reaction, the chloro-bridged analogue is formed in only 8% yield; the main process in the latter case becomes the dealkylation of the amine (HL^{26}) and the formation of the corresponding coordination compound.[105] When $Pd(OAc)_2$ was used, it was possible to synthesise the CPC (XVIIIb) from *NN*-diethyl-*o*-toluidine (see above), while on treatment with Li_2PdCl_4 the above ligand is not cyclopalladated at all.

The possibility of the formation of not only the usual dinuclear but also of trinuclear cyclopalladated compounds should be noted as one of the complications associated with the use of the trimeric palladium(II) acetate for cyclopalladation. Thus, in a more detailed study of the structure of the primary product of the palladation of *NN*-dimethyl-*o*-toluidine, to which a dimeric formula had been attributed earlier[105,106] using mass-spectrometry, ^1H and ^{13}C NMR, and also specific synthesis, it was shown that the true structure of the complex formed in the reaction of (HL^{26}) with $\{Pd(OAc)_2\}_3$ in acetic acid is trinuclear with two pairs of bridging acetate ligands linking three palladium(II) atoms, two of which (the terminal atoms) are *CN*-chelated by the ligand (L^{26}).[182] This type of trinuclear structure was first established for the products of the cyclometallation of dimethylneopentylamine,[131] whose molecular weight in benzene corresponds to the trimer.

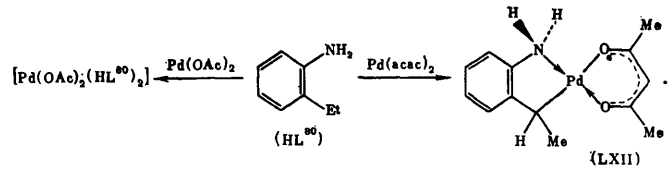
The use of the palladium(II) bis(acetylacetonate) complex as the palladating agent yielded unique results. In particular, with the aid of this reagent it has been possible to obtain the cyclopalladated complex (LX) based on the primary benzylamine,[137] whose metallation presents considerable difficulties:[45]



(LXI) (LX)

It has been suggested[137] that one of the causes of the successful cyclopalladation of this ligand may be the fact that $Pd(acac)_2$ fixes only one amine molecule. Furthermore, the intermediate (LXI) formed in the first stage contains a fairly labile C-bound acetylacetonate ligand, which functions as an effective proton acceptor, stimulating thereby the cyclopalladation reaction.

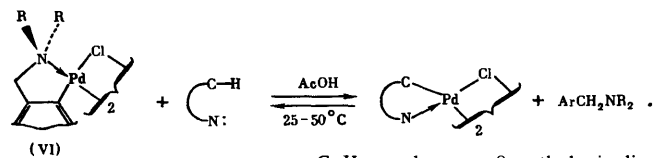
The cyclopalladation of primary *o*-alkylanilines presents special difficulties, since these ligands contain a "poor" coordinating centre (the primary aromatic amino-group) and an aliphatic fragment (the *o*-alkyl group—see above) which is difficult to metallate. Nevertheless, when palladium(II) acetylacetonate was used, it proved possible to achieve the cyclopalladation of *o*-ethylaniline (HL^{80}) at the secondary carbon atom with formation of the CPC (LXII):[137,157]



(HL^{80}) (LXII)

We may note that palladium(II) bis(hexafluoroacetylacetonate) has also been used successfully as a palladating agent[138] with the aid of which it has been possible to obtain CPC based on a wide variety of ligands: tertiary arylalkylamines, Schiff bases, thioamides, thioketones, and also thioethers, especially benzyl methyl sulphide, whose cyclopalladation presents certain difficulties[58] (see above).

A new method of synthesis of CPC, proposed by Yatsimirskii and Ryabov[90,183] and based on the ligand exchange reaction, is of undoubted interest. The fundamental difference from the procedures involving the direct cyclopalladation examined above consists in the use as the palladating agent of any available soluble *ortho*-palladated dimeric complex [for example, compounds (VIa, g)]:



(VI)

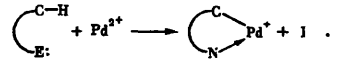
Ar = Ph, R = Me (VIa), or Et (VIg);
Ar = ferrocenyl, R = Me

C–H = azobenzene, 8-methylquinoline, N: benzylideneaniline, 2-benzoylpyridine, *NN*-diethyl-4-nitrobenzylamine

The ligand exchange reactions proceed under comparatively mild conditions (25–50 °C) but have to be carried out in the presence of acetic acid as the cosolvent. Among the CPC obtained by this method, compounds based on 2-benzyl- and 2-benzoyl-pyridine, containing six-membered metallocycles, and the complex with *NN*-diethyl-4-nitrobenzylamine merit special attention. The *ortho*-palladation of the last ligand, containing a benzene ring deactivated by an electron-accepting substituent, was achieved for the first time; this result makes it possible to regard the ligand exchange method as promising for the synthesis of metallocycles which are difficult to obtain under the conditions of the standard methods.

2. The Role of the Base in the Cyclopalladation Process

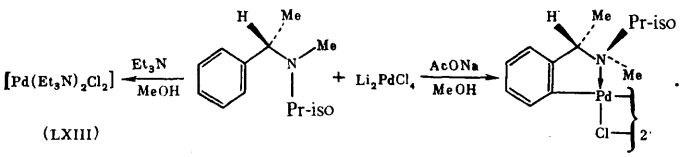
Cyclometallation in the reactions of the type considered here is coupled with the elimination of a proton from the ligand molecule:



When the proton is evolved in the form a strong acid such as HCl, the problem of its neutralisation becomes especially acute. Sodium acetate[46,56,169,184–186] or aliphatic tertiary amines (for example, Et_3N and Bu_3N)[13,45,165] are usually

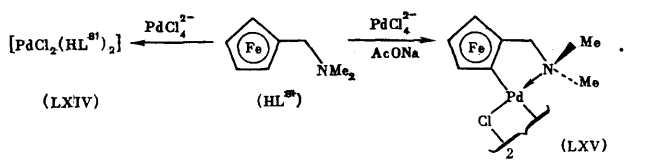
employed as the acceptor; in the cyclometallation of compounds with activated tertiary carbon atoms, K_2CO_3 has been used successfully as the base;[23] if the ligand has very marked basic properties, then an excess of this type of organic substrate is used to neutralise the HCl.[13,45,75]

Tertiary amines are apparently less universal as bases than sodium acetate. For example, in the cyclopalladation of sterically hindered tertiary α-arylalkylamines using triethylamine as the base, the latter competes successfully with the basic substrate for the metal and the main reaction product is its coordination compound (LXIII);[187] we may note that in the presence of sodium acetate such amines readily form CPC:[128,188]



(LXIII)

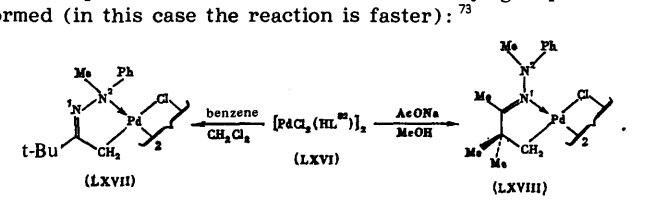
Many systems are known in which the formation of cyclopalladated products in the absence of a base takes place with extremely low yields or the reaction does not occur at all. For example, the cyclopalladation of ferrocenyl ligands in the cyclopentadiene ring can in many cases be achieved only in the presence of sodium acetate despite the fact that this type of ring is more enriched in electrons than the corresponding phenyl derivatives.[46,169,184] Thus, whereas benzyldimethylamine forms the *ortho*-palladation product on treatment with Li_2PdCl_4 in the absence of a base (albeit with a low yield of 35%[45]), its ferrocenyl analogue (HL^{81}) affords under these conditions only the coordination compound (LXIV),[169,189] while the CPC (LXV) is formed only after the introduction of an additional base—sodium acetate:



(LXIV) (HL^{81}) (LXV)

Analogous features have been observed when the results of the cyclopalladation reactions of 2-phenylpyridine[190] and 2-ferrocenylpyridine[184] were compared. Only in the presence of a base (sodium acetate), was it possible to obtain the CPC from a series of acetylhydrazones,[185,191] oximes,[72,125,126] pyrazoles,[192] and phosphines.[56,144]

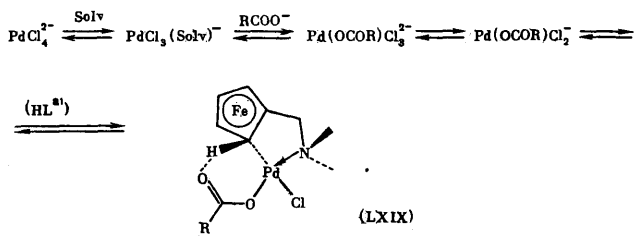
In the cyclopalladation of the pinacolone *N*-methyl-*N*-phenylhydrazone (HL^{82}), the introduction of the base not only accelerates the metallation reaction but also alters its pathway. The intermediate dinuclear coordination compound (LXVI) with the *N*(1)-coordinated hydrazone in the absence of a base in non-polar solvents (benzene, dichloromethane) is slowly and spontaneously metallated at the CMe group and is converted into the CPC (LXVII), while in the presence of a base (sodium acetate) in methanol, the isomeric complex (LVIII) with a metallated t-butyl group is formed (in this case the reaction is faster):[73]



(LXVII) (LXVI) (LXVIII)

The structure of the two isomeric compounds (LXVII) and (LXVIII) has been confirmed by XRA.[193] The authors explained the change in the regioselectivity of this process as a function of experimental conditions by assuming that the complex (LXVI) with the *N*(1)-coordinated ligand (most of the initial hydrazone is bound in this form) participates in the reaction in the presence of a base; in the absence of a base, only the complex with the *N*(2)-coordinated ligand (present in the equilibrium mixture in a small amount) reacts, since the palladation then proceeds at the more active C–CH_3 group adjoining the azomethine bond.[73]

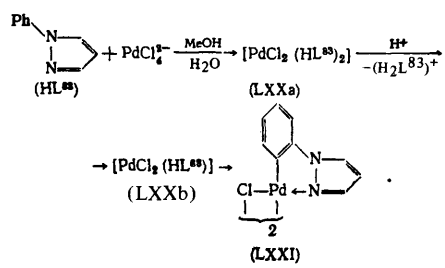
The role of sodium acetate in the cyclometallation reaction is apparently not limited to the simple neutralisation of HCl. When optically active salts of *N*-acetyl-α-aminoacids are used as bases, the cyclopalladated complex derived from *NN*-dimethyl-aminomethylferrocene (HL^{81}) is produced in an optically active form.[46] This example of the enantioselective introduction of planar chirality demonstrates unambiguously that the acid anion is directly involved in the transition state of the cyclopalladation reaction. It has been suggested[46] that the chiral carboxylate ion is inserted in the metallating agent during the cyclopalladation process and then enters into the composition of the bicyclic transition state (LXIX):



(LXIX)

Such asymmetric cyclopalladation reactions have found application in the synthesis of chiral di- and tri-substituted ferrocene derivatives[194] including ferrocenyl analogues of prostaglandins.[12]

There are exceptions to every rule and among cyclopalladation reactions there exists one which does not require the introduction of a base but does proceed in the presence of strong acids. Thus the cyclopalladation of 1-phenylpyrazole (HL^{83}) takes place in methanol in the presence of HCl or $HClO_4$.[43] The authors suggest that the acid is necessary in this case to remove (via protonation) one ligand molecule from the rapidly formed bis-complex (XXIIa). This is accompanied by the formation of the coordination-unsaturated intermediate (LXXb), which is then cyclopalladated with formation of compound (LXXI):



(LXXI)

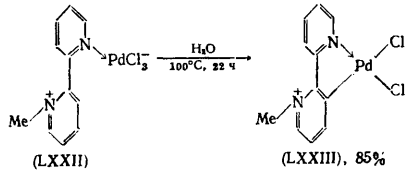
3. Other Experimental Conditions

Reaction conditions such as the nature of the solvent, temperature, and reaction time are quite important in the cyclopalladation of various organic ligands.

The solvent most widely used in reactions of the type considered is methanol.[45,67,72,76,77] Its role does not apparently reduce solely to increasing the solubility of the reactants, in particular, Li_2PdCl_4 and $PdCl_2(PhCN)_2$. The advantages

of polar solvents are probably based on the fact that they promote the creation of vacant sites in the coordination sphere of palladium(II) as a result of solvation. To illustrate this solvent effect, manifested in the stage involving the transition from the coordination compound to the cyclopalladated compound, one may recall the *ortho*-palladation of azobenzene[48] (see above), whose coordination complex is stable in non-polar solvents but is converted into the cyclopalladated compound after the simple addition of alcohol or aqueous dioxan.

The conversion of the palladium(II) coordination complex with a cationic ligand—*N*-methyl-2,2′-bipyridylium (LXXII)—into the cyclopalladated compound (LXXIII) requires a still more polar (aqueous) medium:

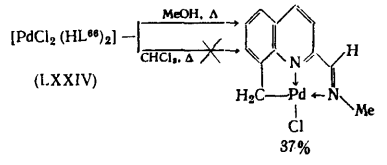


(LXXII) (LXXIII), 85%

Cyclometallation does not occur on refluxing in alcohols (ethanol, 2-methoxyethanol).[134,135]

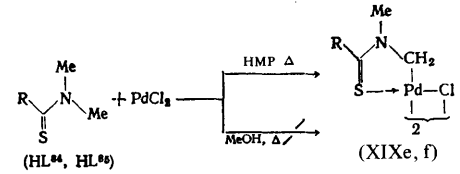
This reaction is especially surprising, since the positively charged pyridinium ring of the ligand is in this instance subjected to *ortho*-palladation (which is traditionally regarded as an electrophilic process).

The successful cyclopalladation of 8-methylquinoline-2-carboxaldimine (HL[66]), forming part of the composition of the coordination compound (LXXIV), in methanol and the absence of metallation products in chloroform (even at elevated temperatures) has been explained[76] as follows: by liberating a vacant site in the coordination sphere of palladium(II), methanol promotes the bidentate coordination of the ligand to the metal, which ensures the equatorial position of the 8-methyl group, necessary for the cyclopalladation in this fragment:



(LXXIV) 37%

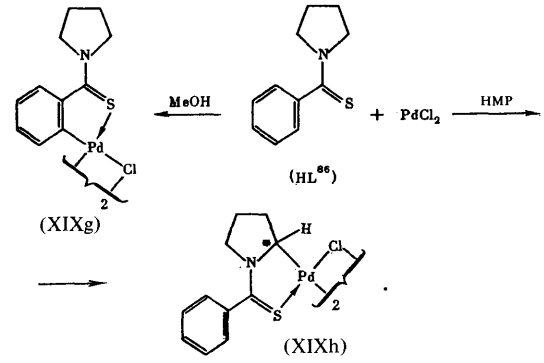
A similar solvation effect is probably the basis of the ready cyclopalladation in hexamethylphosphoramide (HMP) of certain thioamide ligands [for example, (HL[84]) and (HL[85])], which do not enter into this reaction in other solvents, especially in methanol:[67]



(HL[84], HL[85]) (XIXe, f)

R = PhCH=CH [(HL[84]), (XIXe)], —[(HL[85]), (XIXf)]

The nature of the solvent can influence not only the yield of the final product but also the pathway in the cyclopalladation reaction. For example, the cyclopalladation of *N*-thiobenzoylpyrrolidine (HL[86]) in methanol takes place in the aromatic ring with formation of the *ortho*-palladated complex (XIXg), whereas in HMP the α-methylene group of the pyrrolidine ring is subjected to metallation, affording compound (XIXh):[67,195,196]

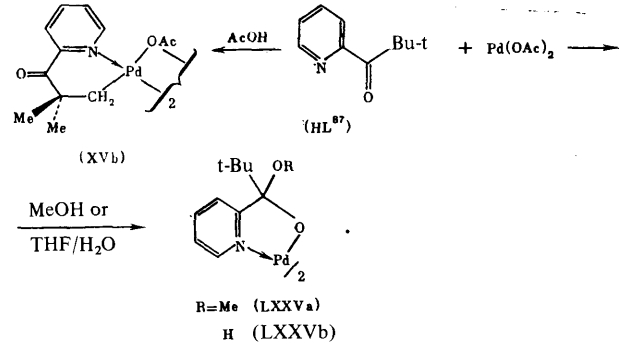


(XIXg) (HL[86]) (XIXh)

The successful resolution of the latter complex into enantiomers constitutes the best proof that the aliphatic fragment of the (HL[86]) is cyclopalladated.[195,196]

Apart from methanol and HMP, which have already been mentioned, some workers use aqueous dioxan[48,197] or 2-methoxyethanol[102] as effectively solvating solvents. Despite all the advantages of polar solvents, certain ligands are sufficiently reactive to enter into the cyclopalladation reaction even in weakly solvating solvents of low polarity such as benzene[137] and chloroform;[75,156] the reactions with palladium(II) acetate are carried out as a rule in glacial acetic acid.[89,172,173,198]

The importance of the correct selection of the solvent is illustrated by the following example. When the reaction of 2-pivaloylpyridine (HL[87]) with $Pd(OAc)_2$ is carried out in acetic acid, the usual dimeric cyclopalladation product (XVb) is formed,[94] whereas in methanol and in aqueous tetrahydrofuran (THF) the bis-chelates (LXXVa) and (LXXVb) are formed respectively as a result of the nucleophilic attack by the methoxide or hydroxide ions on the coordinated acyl fragment of the ligand (HL[87]):[199]

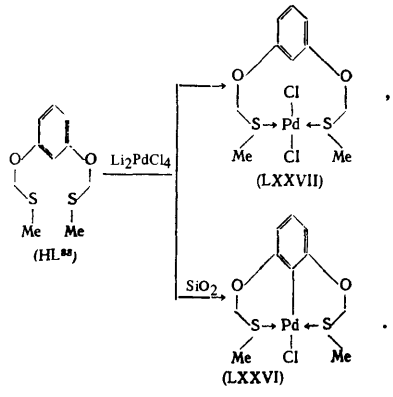


(XVb) (HL[87])

The required cyclometallation reaction time and temperature are determined by many factors: the class of ligand, its stereochemical characteristics, the nature of the palladating agent and solvent, etc. For example, whereas the *ortho*-palladation of the substituted benzylamine (HL[71]) in the aromatic ring activated by donor substituents takes place almost instantaneously even at −78 °C[165] (see Section IV), the cyclopalladation of *NN*-diethylthiobenzamide (HL[29]) is possible only after prolonged heating in HMP.[67] It is noteworthy that the increase in the reaction temperature and time frequently does not produce the desired result owing to the progressive formation of palladium black or the occurrence of other side processes.

Yet another way whereby the cyclopalladation reaction can be accelerated significantly and which is based on the catalytic action of silica gel merits mention.[62] As an example,

we shall quote the results of two attempts at the cyclopalladation of the bis-thioether ligand (HL^{88}): when the reaction with Li_2PdCl_4 is carried out in the presence of silica gel, the CPC (LXXVI) is formed in 95% yield, whereas in the absence of the Lewis acid under the same conditions the main reaction product is the coordination complex (LXXVII):[62]



Thus analysis of the literature data indicates a wide variety of factors influencing the mode and ease of the cyclopalladation reactions and also the structure of the cyclopalladated complex formed. However, a more far-reaching and detailed study of the causes of such effects and the mechanisms of reactions of the given type constitutes at the present time a task of fairly considerable current interest.

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During the preparation of the manuscript for publication, a number of communications having a direct bearing on the topic of this review appeared in the literature.

Apart from the annual compilations of articles on the chemistry of palladium compounds,[200,201] Omae's monograph, summarising a series of review articles by the author published previously,[28,30,37-42] was published;[202] a review of this book[203] contains a series of serious critical comments.

Recently, there has been some progress in the research into the mechanisms of cyclopalladation reactions. It has been demonstrated by spectroscopic and kinetic studies of the *ortho*-palladation of a series of ring-substituted *NN*-dialkylbenzylamines that the reaction mechanism depends significantly on the nature of the solvent: in acetic acid, the rate-limiting stage is the opening of the acetate bridges in the polynuclear palladium acetate, while in chloroform the palladation proper of the amine takes place in the rate-determining stage within the framework of a pseudotricoordinate 14-electron intermediate.[204] The study of the kinetics and mechanism of the ortho-palladation of a series of 3,2′-annelated 2-phenylpyridines with bridges of different lengths by palladium bis(diketonates) suggested that the rate-determining stage of the process is not the attack by palladium(II) on the benzene ring but the subsequent deprotonation.[205]

The cyclopalladated ligand exchange reactions are finding increasing application in the synthesis of CPC of various types;[206-209] an advantage of this method is the preferential palladation of the more electron-accepting of the two ligands in the equilibrium process.[210,211] However, the ideas about the reaction mechanisms still remain contradictory: together with the dissociative mechanism, proposed on the basis of the study of the kinetics and thermodynamics of the reactions,[211,212] the possibility of the formation of mixed-ligand mononuclear bis-chelate CPC as key intermediates has also been discussed.[210] The final result is determined in both cases by the comparative stabilities of the Pd–C σ-bonds of the two palladium-containing heterocycles in relation to protonolysis.[213]

The problem of estimating the influence of various structural factors on the ease of cyclopalladation remains of current interest. Comparison of the behaviour of 1-phenyl- and 1-benzyl-substituted pyrazoles[214] and bornanopyrazoles[215] in the *ortho*-palladation reactions confirms the greater ease of formation of complexes with five-membered metallocycles: the 1-phenyl derivatives readily form CPC by reaction not only with palladium(II) acetate but also with Li_2PdCl_4, while 1-benzyl-substituted ligands afford only the coordination complexes. At the same time an increasing number of communications contradicting the idea of the absolute preference for five-membered palladium-containing heterocycles have been published. Thus the cyclopalladation of *N*-phenylbenzamidine by both $Pd(OAc)_2$ and Li_2PdCl_4 results in the formation of CPC with six-membered metallocycles as a result of metallation in the aniline ring and not the benzamidine ring, which might have led to the formation of a five-membered palladium-containing metallocycle; it has been suggested that this reaction pathway is caused by the greater electron density in the benzene ring of the aniline fragment.[216] For comparison, we may note that the *ortho*-palladation of substituted benzylideneanilines takes place in the aromatic ring of the benzylidene fragment.[217-219] An even more surprising result has been obtained in a study of the cyclopalladation of a series of benzylideneamines of the type $2,4,6\text{-}Me_3C_6H_2CH = N(CH_2)_nPh$ ($n = 0,1,2$),[220] which make it possible to compare simultaneously the tendencies towards metallation at the sp^2- and sp^3-centres and to estimate the importance of the size of the palladium-containing metallocycle formed. It was shown that in all the systems the metallation takes place at the *ortho*-methyl group (sp^3-centre) with formation of a six-membered palladium-containing metallocycle even if the alternative pathway involving metallation in the *ortho*-position in the benzene ring of the amine fragment (sp^2-centre) should have led to the formation of a five-membered ring (for $n = 1$). The nature of the factors which can compensate for the five-membered ring being preferred (compared with the six-membered ring) and for the preferred metallation of the sp^2-centre (compared with the sp^3-centre) remains obscure.[220]

The formation of six-membered metallocycles can be stimulated by introducing an additional (second) heterodonor centre: in contrast to the potentially bidentate 2-(1-methylbenzyl)pyridine, which is not metallated by $PdCl_4^{2-}$, the corresponding 2,2′-bipyridyl derivative readily forms a CPC with a tridentate *NNC*-coordinated ligand on treatment with Na_2PdCl_4 in aqueous HCl;[221] the structure of the complex has been confirmed by X-ray diffraction. It is suggested that the ready formation of CPC with six-membered palladium-containing metallocycles by potentially tridentate ligands of the NCN type {for example, 1,3-bis[1-(2-pyridinyl)-ethyl]benzene} is stimulated by the fact that metallation removes the stresses arising in the stage involving simple coordination via the terminal heterodonor centres.[222] We may note, within the framework of tricyclic systems with ligands of the CNNC type, the formation of not only six-membered but also seven-membered palladium-containing metallocycles proved to be possible.[223]

The possibilities arising from the modification of the cyclopalladation conditions for ligands with unfavourable structural features have been demonstrated in a number of investigations. As an illustration of the greater effectiveness of palladium(II) acetate compared with tetrachloropalladates,

one may mention that with its aid it has been possible to achieve the *ortho*-palladation of sterically unhindered benzyl methyl sulphide[224] and methyl α-naphthyl sulphide[225] and also the cyclopalladation in the aliphatic carbon centres of 2-t-butylbenzothiazole[226] and substituted benzylideneazine $(2,4,6\text{-}Me_3C_6H_2CH{=}N)_2$;[207] six-membered palladium-containing metallocycles are formed in the last case. Cyclopalladated complexes belonging to the series of substituted benzylidenebenzylamines have been synthesised in satisfactory yields by reaction with Li_2PdCl_4 only for a 1:1 reactant ratio, while in the case where a twofold excess of the ligand was used only the coordination complexes of the corresponding benzylamines were isolated as a result of hydrolysis.[227] With the same 1:1 stoichiometry and using $PdCl_2$ as the palladating agent, it has been possible to synthesise the CPC of substituted benzoylbenzylideneanilines.[228] An interesting example of the change in the metallation pathway as a function of the nature of the solvent is provided by two investigations:[211,212] when the reaction of the dibenzylamine ligand having two potential metallation regions, i.e. $3,4\text{-}(MeO)_2C_6H_3CH_2N(Me)CH_2C_6H_4NO_2\text{-}4$, with palladium(II) acetate is carried out in chloroform, the electron-enriched benzene ring is palladated, while in acetic acid the reaction involves the benzene ring containing the electron-accepting nitro-group. In the *ortho*-palladation reaction of α-phenyl-α-(2-pyridyl)toluene on treatment with palladium(II) acetate, a CPC with a six-membered palladium-containing metallocycle is formed only in acetic acid, while in benzene the reaction stops after the formation of the simple coordination *trans*-bis-complex.[229] The conversion of such coordination intermediates into CPC can be achieved either by heating in a suitable solvent—for example, chloroform[230] or ethanol[221]—or by introducing an additional equivalent of the palladating agent—for example, Li_2PdCl_4[215] or $PdCl_2$.[231] The synthesis of unusual dinuclear CPC with a single halide bridge from the *NCN*-chelated 2,6-bis(dimethylaminomethyl)phenyl ligand deserves to be mentioned.[232]

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Photochemical Methods for the Construction of an Additional Four-membered Carbocycle in Steroids

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The photochemical methods for the synthesis of pentacyclic steroids with an additional four-membered carbocycle are considered. A systematic account is given of the available literature data on the [2 + 2] photocycloaddition of steroid enones and dienones to various alkenes and alkynes and also on the dimerisation of dienones and intramolecular cyclisation of steroid ketones.
The mechanism of the photolytic reactions is discussed and the stereo- and regio-specificity of the photocycloaddition are considered as a function of the structure of both the steroid and the alkene. It is shown that the pentacyclic steroids obtained are convenient intermediates for further modifications.
The bibliography includes 106 references.

CONTENTS

I. Introduction 270
II. Photocycloaddition of alkenes to steroid enones 270
III. Photocycloaddition of alkynes to αβ-unsaturated ketosteroids 275
IV. Photodimerisation of steroid dienones 276
V. Photocycloaddition of alkenes to steroid dienones 276
VI. Photocycloaddition of dienes to steroid dienones 278
VII. Intramolecular photocyclisation of steroid ketones 280

I. INTRODUCTION

In the chemistry of steroid hormones, the modification of the skeleton of natural steroids is used to obtain compounds having a narrower and specific spectrum of biological activity, which gives rise to the possibility of their practical application. Among the numerous types of such transformed steroids, compounds containing an additional carbocycle are of great interest. The methods of their synthesis are fairly varied.

This review is devoted to the photochemical method of synthesis of steroids condensed with an additional four-membered carbocycle. Such pentaranes† exhibit an enhanced hormonal activity in many instances[2-15] and are also convenient intermediates for further modifications of the steroid skeleton.[16-22] Only the photochemical methods of synthesis of pentaranes are considered, because these methods frequently constitute almost the only possibility of the construction of a four-membered ring and the contribution of other methods of synthesis of similar structures (such as, for example, the cycloaddition of dichloroketen to steroid alkenes[23-26] or the intramolecular cyclisation of tosylates[27-29]) is small.

Photochemical [2 + 2]cycloaddition is a general method for the construction of pentacyclic steroids and, in contrast to the dark reactions, makes it possible to introduce the cyclobutane fragment into any site in the steroid molecule.

The main aim of the review is to demonstrate the synthetic possibilities of photochemical cyclisation to pentaranes and its stereo- and regio-specificity as a function of the structure of the steroid and alkene; special factors associated with the mechanism of the photoexcitation of the reacting molecules, their electronic state, etc. will not be discussed in detail. These questions have been dealt with quite fully in other publications.[30-34] The review contains data mainly referring to the last 18 years. Some information about the synthesis of cyclobutanosteroids up to 1970 can be found in a monograph.[35]

II. PHOTOCYCLOADDITION OF ALKENES TO STEROID ENONES

The interaction of photochemically excited enones and dienones with alkenes or alkynes usually leads to the formation of a four-membered carbocycle and frequently constitutes the most convenient or even the only available method of synthesis of such structures. In the steroid chemistry, the photocyclo-addition of various alkenes to αβ-unsaturated ketones# is a well-developed and convenient method for the introduction into the steroid molecule of an additional four-membered carbocycle, which is widely used at the present time.[36] Here it has been shown that this reaction leads to the formation of both *cis*-αα- and *trans*-αβ-cyclobutanes; insignificant amounts of the *cis*-ββ-isomers arising simultaneously are attributed to the epimerisation of *trans*-αβ-cyclobutanes under the reaction conditions.[37] The stereochemistry of the photoannelation can be explained on the basis of the general features of the interaction of an excited enone with an alkene in the ground electronic state: the attack by the latter takes place from the sterically less hindered α-region of the enone; (2) the *trans*-cyclobutane is formed as a result of the conformational inversion of the intermediate 1,4-biradical.[37-42]

The photocycloaddition of various alkenes to derivatives of testosterone (I) has been investigated[37] (Scheme 1); the yields of the isomeric cyclobutanosteroids (II)–(IV) obtained are listed in Table 1.

†The name "pentaranes"[1] is used for pentacyclic steroids containing an additional carbocycle.

#Here and henceforth we shall use the term "addition of alkenes (or olefins) to the more bulky steroid molecule".

Scheme 1

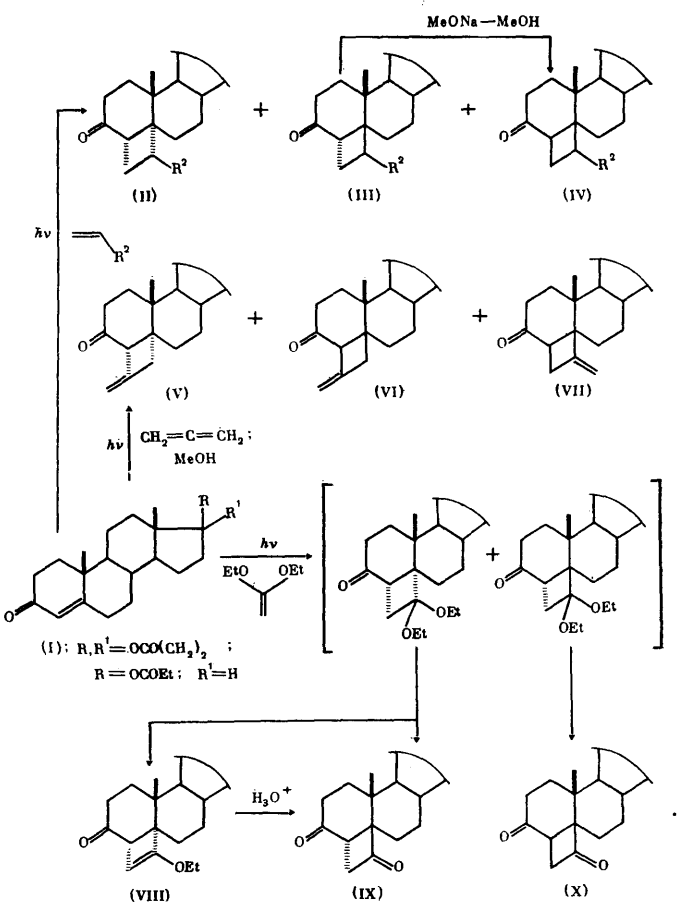


Table 1. The yields of the cyclobutanosteroids (II)–(IV).[37]

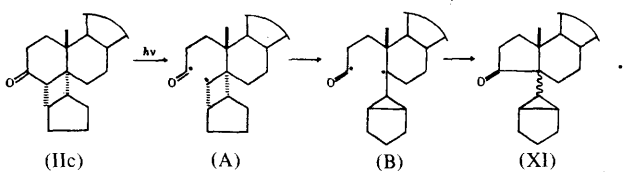
Olefin	Cyclic adduct, %		
	4α, 5α-(II)	4α, 5β-(III)	4β, 5β-(IV)
Ethylene	57	24—30	traces
Isobutene	76	12	traces
Cyclopentene	43	35	9
1-Acetoxycyclopentene	30	35	traces
Cyclohexene	40	25	12

It follows from the Table that ethylene adds to the steroid enone (I) affording the cyclic adducts (IIa) and (IIIa) with a high overall yield (81–87%), 4α,5α-cyclobutane (IIa) predominating in the mixture. Irradiation of a methanolic or ethyl acetate solution of testosterone propionate and ethylene also affords a mixture of compounds (IIa) and (IIIa) together with a small amount of the 4β,5β-epimer (IVa).[38,43] The high yields of the products of the reaction of the enone (I) with ethylene, which is a relatively unreactive alkene, can be explained by the fact that the steroid enone gives rise to a long-lived triplet state on irradiation.[44] In the reaction with a more electron-enriched alkene—isobutene—higher yields of 4α,5α-cyclobutane (IIb) were obtained. It was noted that the reactions with geminally substituted alkenes give rise only to cyclic adducts of the "head to tail" type (HT), while the reaction with cyclic alkenes affords only the *anti*-adducts,[37] although there are data[43] indicating the isolation of both the *syn*- and *anti*-isomers of the cyclic adduct of compound (I) with cyclopentene. The addition of allene to the enone (I) gives rise to a 5 : 1 mixture of compounds (V) and (VI); the reduction of the reaction temperature to −70 °C results in the exclusive formation of compound (V).[43]

In order to account for the high structural specificity of the given reaction, the empirical "Corey rule"[45] that the "enone-unsaturated substrate" exciplex plays a decisive role, which has been developed for the series of aliphatic and monocyclic αβ-unsaturated ketones, has been successfully resorted to.[37]

The addition of 1,1-diethoxyethylene to compound (I) leads to a mixture of labile primary cyclic *cis*-4α,5α- and *trans*-4α,5β-adducts, which have been characterised as the cyclobutene (VIII) and the ketones (IX) and (X) (Scheme 1).[37]

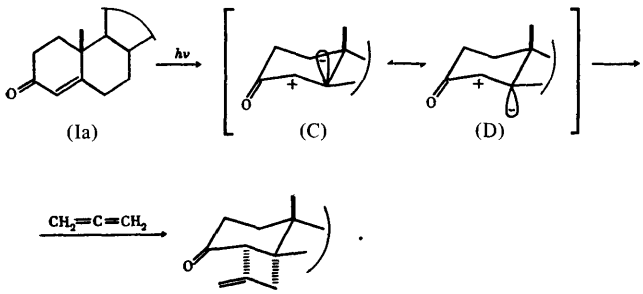
It is of interest to note that 5-cyclopropyl-A-norsteroid (XI) has been isolated as a side product from the mixture of products of reaction of compound (I) with cyclopentene. The appearance of this steroid has been explained by the Norrish type (I) cleavage of cis-4α,5α-cyclobutane (IIc) with formation of the acylcyclobutyl biradical (A), which then rearranges to the cyclopropyl-substituted biradical (B) with subsequent stabilisation by conversion to the final compound (XI):[37]



Extremely interesting results concerning the inversion of the stereospecificity of the photocycloaddition of alkenes to αβ-unsaturated ketones have been recently obtained by de Mayo.[43,46] It was found that irradiation of alkenes and testosterone or its propionate (I, R = OH or OCOEt), adsorbed on SiO_2 or Al_2O_3, leads to the preferential approach by the alkene to the β-region of the steroid molecule because the α-region is to a large extent blocked by the adsorbent molecules as a result of the preliminary adsorption of the steroid enone. It was shown that under these conditions the overall yield of the cycloaddition products increases. Thus, in the case of ethylene (R^2 = H, Scheme 1), the (IIa) : (IVa) = 42 : 58 mixture of cyclobutanes was obtained in a quantitative yield. *trans*-4α,5β-Cyclobutane (IIIa) was isolated only in trace amounts. Analogous results were obtained at a low temperature (−70 °C). The reaction of the testosterone propionate (I) adsorbed on SiO_2 with allene leads to a mixture of cyclic *cis*-4α,5α- and *cis*-4β,5β-adducts in the proportions (V) : (VI) = 1 : 1; the second regioisomer (VII) of the HT type was also isolated in an insignificant amount.[43] Thus the adsorption of the steroid enone on SiO_2 or Al_2O_3 prevents the conformational inversion of the intermediate biradical required for the formation of the *trans*-joined cyclobutanosteroids.

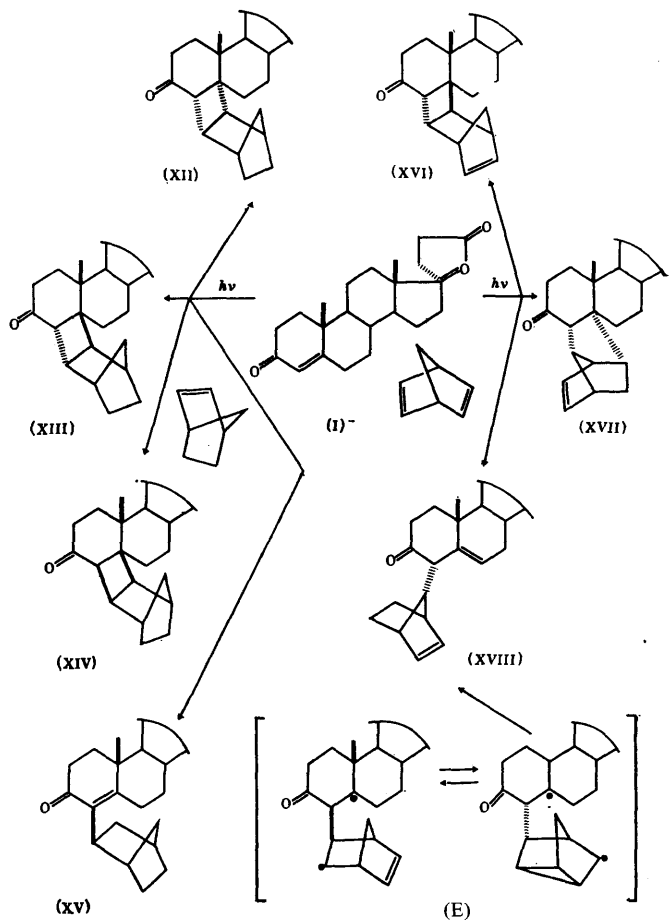
It is noteworthy that the structural specificity of the photocycloaddition of alkenes to αβ-enones is determined in the first place by the conformation of the enone reacting in the triplet state.[47] It has been shown in relation to cholest-4-en-3-one (Ia) that, of the two possible conformations (C) and (D) of the excited enone, the conformation (D) with the *trans*-disposition of the 19-CH_3 group and of the unpaired electron in the *p* orbital at C(5) is preferred. Accordingly, the cyclic adduct of the enone with allene should have a structure of the "head to head" type (HH), and the approach

of allene to the excited enone (Ia) from the α-region becomes preferred:



The addition of norbornene to the steroid enone (I) leads to a mixture of *cis*-4α,5α-cyclobutane (XII) (41%), the *trans*-4α,5β-epimer (XIII) (27%), the *cis*-4β,5β-adduct (XIV) (2%), and the adduct (XV) (17%)[48] (Scheme 2):

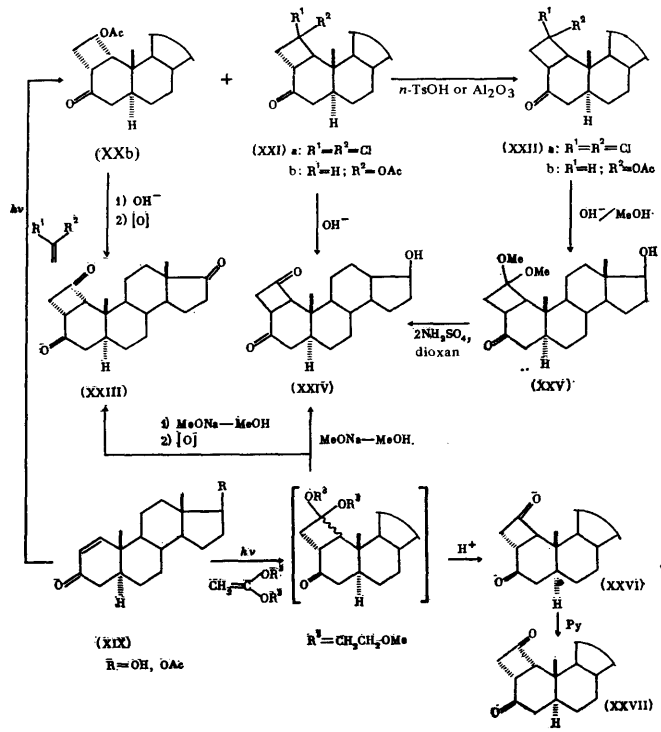
Scheme 2



The last adduct arises as a result of the 1,3-hydride shifts with formation of 4-norbornyl-3-keto-Δ⁵-steroid, which then isomerises to the Δ⁴-3-ketone (XV) in the course of the reaction. The appreciable stability of the *trans*-isomer (XIII) as regards epimerisation has been noted, which has been explained by the character of its conformation (the A ring is in the chair and not the boat form characteristic of the majority of 4α,5β-cyclobutanes,[31] which hinders the approach of the nucleophile to the 3-carbonyl group). The reaction of compound (I) with norbornadiene is fairly complex (cf. McCullough et al.[49]). *trans*-4α,5β-Cyclobutane (XVI) (10%) and two other products—(XVIII) (16%) and (XVIII) (53%)—were isolated from the mixture of substances (see Scheme 2). The formation of the last product has been explained by the steric hindrance to the rotation about the C(4)–C bond in the intermediate biradical (E).[48]

The cyclobutanosteroids condensed with the A ring in the 1- and 2-positions can be obtained by the photocycloaddition of olefins to Δ¹-3-ketosteroids. Literature data indicate a low reactivity of these enones compared with the Δ⁴-3-ketones. Thus it has been shown that ethylene, malic anhydride, and 1,1-difluoroethylene do not add to the series of androstane and pregnane Δ¹-3-ketones investigated.[50] However, irradiation of the Δ¹-3-ketone (XIX) in benzene solution containing 1,1-dichloroethylene led to a 16% yield of the substituted *trans*-1β,2α-cyclobutane (XXIa), which readily undergoes epimerisation at the C(2) centre, affording compound (XXIIa)[50] (Scheme 3). The stereochemistry of compound (XXIa) has been deduced from X-ray diffraction data. The hydrolysis of *trans*-1β,2α-cyclobutane (XXIa) and of its *cis*-1β,2β-isomer (XXIIa) yielded the same *cis*-1β,2β-cyclobutan-1′-one (XXIV). The reaction of the steroid enone (XIX) with vinyl acetate under analogous conditions led to a complex mixture of substances; after chromatographic separation, two products were isolated: *trans*-1β,2α-cyclobutane (XXIb) (21%) and *cis*-1α,2α-cyclobutane (XXb) (2%). Hydrolysis of the latter and subsequent Jones oxidation yielded 1α,2α-cyclobutan-1′-one (XXIII):

Scheme 3



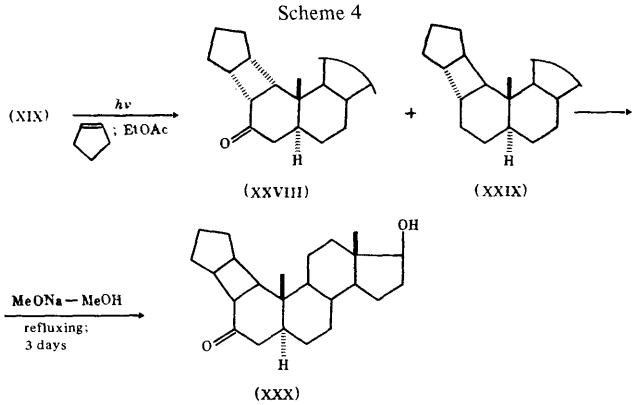
Thus the addition of substituted alkenes to Δ¹-3-keto-steroids leads to the formation of *trans*-cyclobuane adducts of the HT type with high regio- and stereo-specificity.

These adducts readily epimerise at the C(2) centre to form the more stable *cis*-1β,2β-cyclobutanosteroids.

The addition of cyclopentene to compound (XIX) led to the preferential formation of *cis*-1α,2α-cyclobutane (XXVIII) (56%) together with the usual *trans*-isomer (XXIX) (30%)[51]

(Scheme 4):

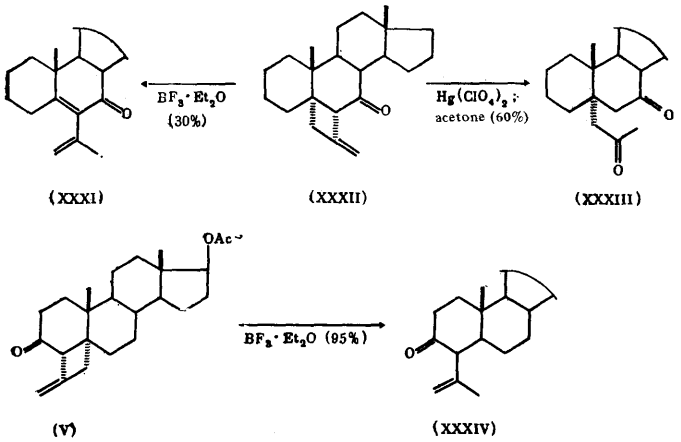
Scheme 4



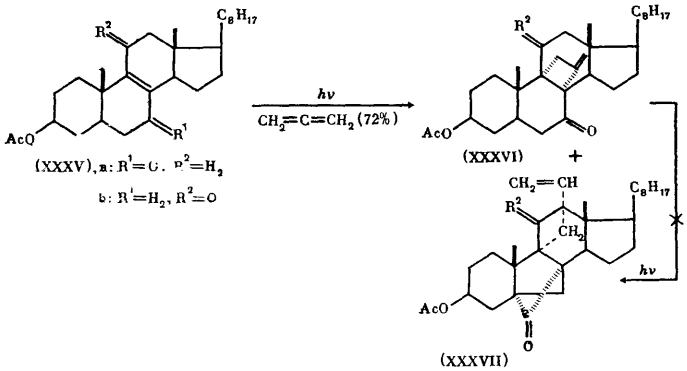
The unusual stability of the last compound as regards epimerisation was noted here: the corresponding *cis*-1β,2β-isomer (XXX) was obtained only after prolonged refluxing of compound (XXIX) with MeONa in methanol. The isomeric 1β,2α-, 1α,2α-, and 1β,2β-cyclobutanones (XXVI), (XXVII), and (XXIV) were also obtained by adding ketene bis(2-methoxyethyl)acetal to compound (XIX) [51,52] (see Scheme 3). It is of interest to note that, whereas the acid-catalysed epimerisation of the *trans*-diketone (XXVI) leads to an equimolar mixture of compounds (XXIV) and (XXVII), heating of compound (XXVI) in pyridine affords only the *cis*-1α,2α-cyclobutanone (XXVII). [51]

Steroid enones substituted in the Δ^1-bond, for example the acetate of 17β-hydroxy-2-methyl-5α-androst-3-one, do not form cyclic photoadducts by reaction with alkenes at all, [50] which agrees with Corey's observation that such photochemical reactions are difficult for C(2)-substituted enones. [45]

6'-Methylene-5α,6α-cyclobutano-7-ketosteroid (XXXII) has also been described and its cleavage under various conditions has been investigated. [53,54] For example, when compound (XXXII) is refluxed in benzene in the presence of an excess of BF_3 etherate, the 6-isopropenyl-substituted 7-ketone (XXXI) is formed. Under analogous conditions, 4'-methylene-4α,5α-cyclobutane (V) gives rise to a high yield of the 4-isopropenyl-substituted 3-ketone (XXXIV). These products are apparently formed as a result of the electrophilic attack by the BF_3 etherate on the exocyclic methylene bond with subsequent opening of the cyclobutane ring. [53] The cleavage of methylenecyclobutane (XXXII) with mercury perchlorate in acetone leads to the diketone (XXXIII) in 60% yield. [54] These examples clearly demonstrate the possibility of using cyclobutanosteroids as intermediates for the transformation of steroids.



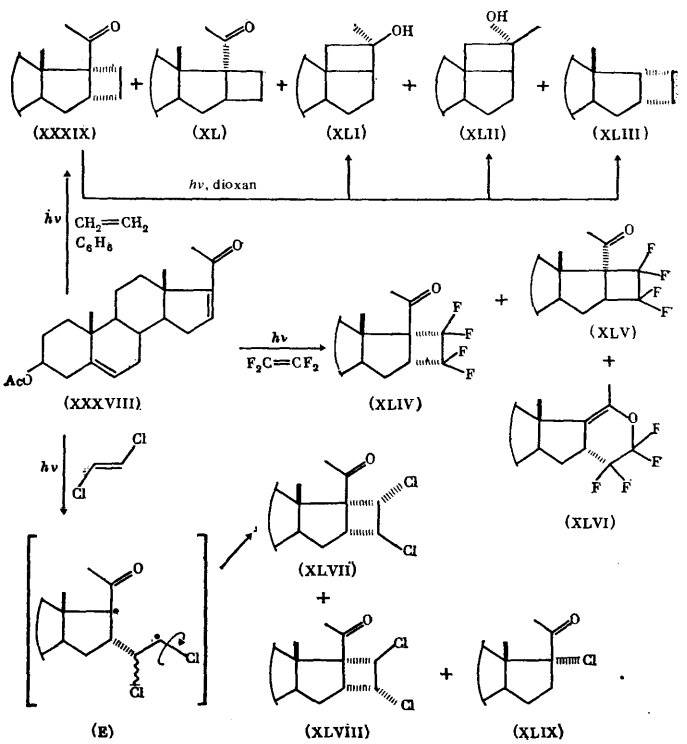
The 8α,9α-cyclobutanosteroid (XXXVI) has been obtained by the photoaddition of allene to 7-keto-$\Delta^{8(9)}$cholestene (XXXVa). The structure of the ketone (XXXVII) was attributed to the second compound arising under these conditions in ~20% yield:



Under analogous conditions, 11-keto-$\Delta^{8(9)}$-cholestene (XXXVb) does not react with allene. [55]

The 16-dehydro-20-keto-group in pregnanes is fairly reactive in photocycloaddition to various alkenes, which makes it possible to obtain the corresponding 16,17-cyclobutanosteroids. The first studies on their synthesis with participation of ethylene and its derivatives were published as early as the 1960's [56] and the formation of only *cis*-joined products with a significant predominance of the 16α,17α-isomers was demonstrated. [39,56] Thus, when ethylene is passed into an irradiated benzene solution of 16-dehydropregnenolene acetate (DPA) (XXXVIII), a mixture of 16α,17α- and 16β,17β-cyclobutanes (XXXIX) and (XL) is formed in proportions of ~7:1 (Scheme 5).

Scheme 5

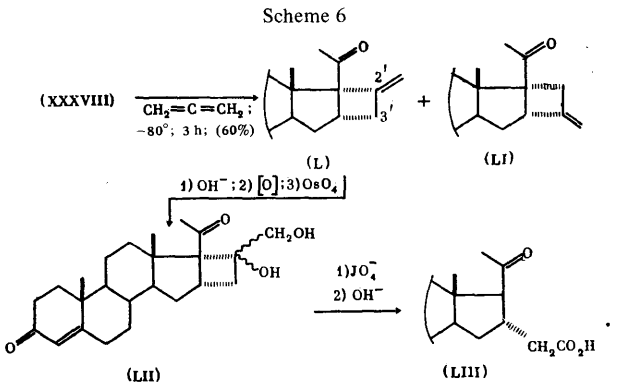


After prolonged irradiation, the cyclobutanols (XLI) and (XLII) and the desacyl compound (XLIII) were detected as additional products in the reaction mixture. They were also obtained by the photolysis of the principal product (XXXIX) in dioxan. Under these conditions, the isomeric 16β,17β-cyclobutane (XL) is stable. The formation of compounds (XLI) and (XLII) was explained by the intramolecular attack on the 20-carbonyl group in an excited state by the vicinal 18-methyl group in the molecule of compound (XXXIX) and the formation of compound (XLIII) was accounted for by the abstraction of the acyl group. When the reaction is carried out in methanol, the yield and fraction of the main cyclic adduct (XXXIX) increased to 90%. When ethylene is passed through DPA absorbed on anhydrous SiO_2 at −70 °C, the overall yield of cyclic adducts rises to 70–85% with the simultaneous change in their stereochemistry in favour of an increase in the amount of the ββ-isomer: (XXXIX)/(XL) ≅ 1:1.[43]

A high stereoselectivity of the cycloaddition has been observed also for the reaction of DPA with substituted alkenes,[2,39,57] which leads, for example, in the case of tetrafluoroethylene,[39] to a mixture of cyclic αα- and ββ-adducts (XLIV) and (XLV) in proportions of ~2:1 together with the formation of very small amounts of the dihydropyran (XLVI). The addition of *cis*- or *trans*-dichloroethylene to compound (XXXVIII) yields a mixture of substances of identical composition, from which *trans*-16α,17α-dichloro-compounds (XLVII) and (XLVIII) were isolated in proportions of ~1:1, differing in the configuration of the chlorine atoms. The 17α-chloropregnenolene (XLIX), detected in a very small amount, is apparently formed as a result of the direct addition of HCl to the initial enone (XXXVIII).[39] The fact that the *cis*- and *trans*-dichloroethylenes give rise to the same cyclic adduct agrees with the two-stage reaction mechanism via a biradical (F) (see Scheme 5); the rate of formation of the C(17)–CCl bond is evidently comparable to the rate of inversion of the C(2′)–Cl bond.

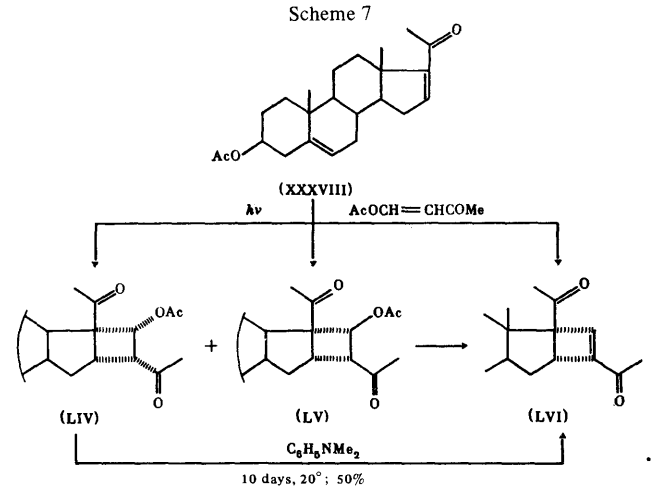
The photochemical reaction of DPA with allene is stereospecific and involves the formation of the 16α,17α-regioisomers (L) and (LI) in proportions of ~5:1 and an overall yield of ~60%[39] (Scheme 6):

Scheme 6



The structures of these compounds have been established with the aid of CD spectra in addition to certain chemical reactions with the main product (L). Thus its hydrolysis with subsequent Oppenauer oxidation afforded the corresponding Δ^4-3-ketone, whose hydroxylation with OsO_4 led to a mixture of diols (LII); successive treatment of these diols with OsO_4 and alkali yielded the familiar acid (LIII), which is formed via an intermediate stage involving the unstable cyclobutanone.[39] The photocycloaddition of 1-acetoxybut-1-en-one to DPA is of interest because both reactants can be in an excited state under the conditions of the photolysis. The cyclic 16α,17α-adducts (LIV) and (LV) in proportions of ~2:1 were then obtained together with a small amount of the cyclobutene (LVI). The latter was obtained after compound (LIV) had been kept for a long time together with dimethylaniline in solution in the $CHCl_3$–methanol mixture, although its diastereoisomer (LV) is stable under these conditions[58] (Scheme 7).

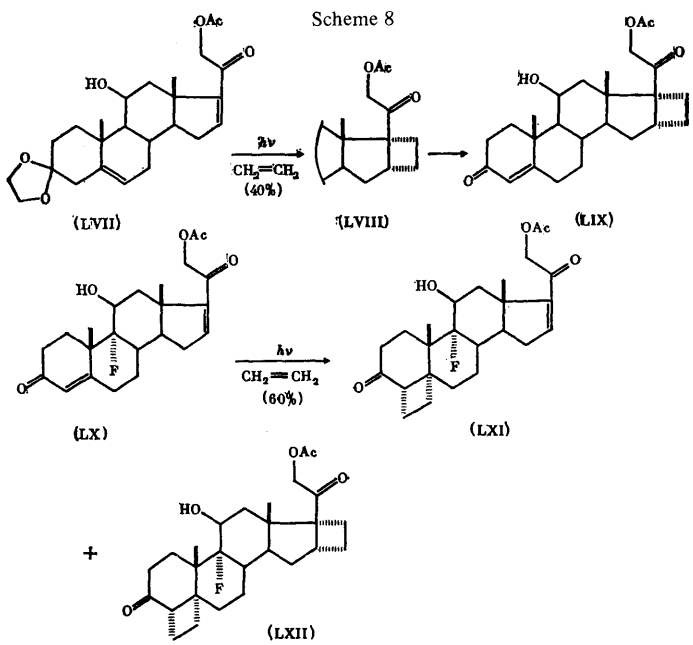
Scheme 7



The observed regiospecificity of the photochemical reaction conflicts with "Corey's rule",[45] because the preferential formation of cyclic adducts of the (EE) type should follow from an examination of the structures of the exciplexes. In order to account for this contradiction, one can postulate that the first reaction stage is the ordered orientation of the initial enones, which are in the ground state, after which the above coordinated complex undergoes photoexcitation with formation of the cyclic adducts (LIV) and (LV).[58]

The presence of substituents in the steroid skeleton of the molecule of compound (XXXVIII) does not reduce its reactivity in the photochemical reaction, but, when the Δ^4-3-keto-group is present together with the Δ^{16}-20-keto-

Scheme 8



group, cycloaddition takes place preferentially with participation of the former group. Thus it has been shown that the interaction of compound (LVII) with ethylene leads to a 40% yield of the 16α,17α-cyclobutane (LVIII), which is converted further into the Δ^4-3-ketone (LIX). On the other hand, the 4α,5α-cyclobutane (LXI) was obtained in 60% yield from the unsaturated 3,20-diketone (LX); the corresponding bis-adduct (LXII) was observed only in trace amounts in the mixture[56] (See Scheme 8).

It is of interest to note that in the monocyclic series cyclopent-2-enones exhibit a greater reactivity than cyclohex-2-enones.[59]

Thus, when account is taken of the data considered above, αβ-unsaturated ketosteroids can be arranged in the following sequence in terms of their reactivity: Δ^4-3-keto- > Δ^{16}-20-keto- > Δ^1-3-keto-. It must be emphasised that this series has been set up on the basis of a fairly limited set of steroid enones and one cannot therefore rule out the possibility that corrections will be introduced in connection with the appearance of new experimental data.

III. PHOTOCYCLOADDITION OF ALKYNES TO αβ-UNSATURATED KETOSTEROIDS

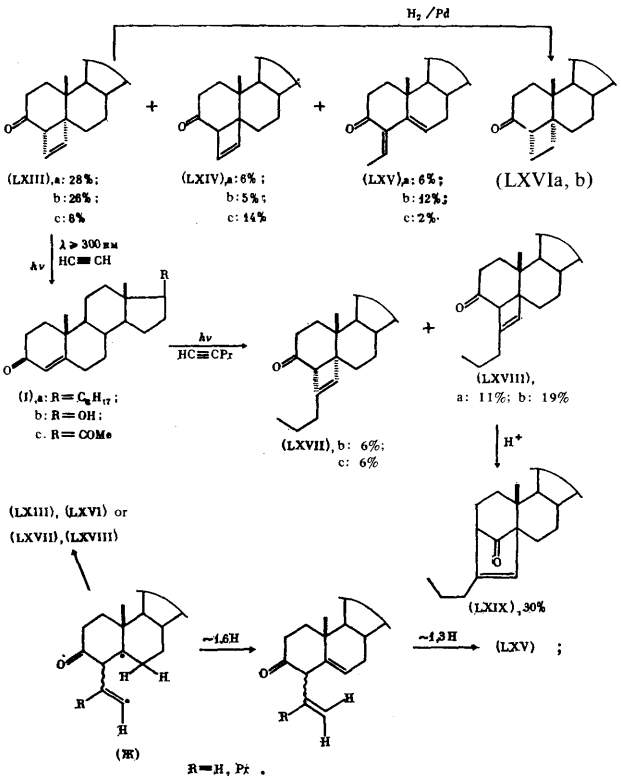
The photocycloaddition of alkynes to steroid enones gives rise to cyhclobutenosteroids with interesting synthetic possibilities. In view of their high strain, such structures undergo various transformations already under the conditions of the photolysis, which, when combined with certain dark reactions, leads to new ways of transforming steroids. Owing to the reduced nucleophilicity of the triple bond, alkynes are less reactive than alkenes in reactions involving addition to the excited enone. For example, it is known that the interaction of 2-cyclohexanone with vinylacetylene involves exclusively the double bond of the latter.[60]

When the steroid enones (Ia, b) are irradiated in ethyl acetate saturated with acetylene, mixtures of the diastereoisomers (LXIIIa, b) and (LXIVa, b) are formed in proportions of ~5:1 and in an overall yield of ~30%;[61] the reaction proved to be less stereoselective than the corresponding reaction with ethylene. On catalytic hydrogenation, the cyclobutenes (LXIIIa, b) afford the corresponding cyclobutanes (LXVIa, b) (Scheme 9).

Together with the cyclic adducts (LXIIIa, b) and (LXIVa, b), the ethylidene derivatives (LXVa, b) were obtained in a yield of ~6–12%. The study of the cycloaddition of acetylene to compounds (Ia, b) under the influence of light with λ ≥ 320 nm, which is absorbed solely by the initial αβ-enone, the intramolecular inversion in the cyclic adduct being ruled out, showed that all three products (LXIII)–(LXV) are also formed under these conditions, from which the authors concluded that the reaction leads immediately to both diastereoisomers.[61] Analogous results were achieved in the photolysis of compound (Ib) together with pent-1-yne, which leads to stereoisomers of the type (LXVIIb) and (LXVIIIb).[62] The mechanism proposed for their formation, via the intermediate biradical (G) stabilised as a result of its closure to form cyclobutene or by disproportionation to 1,4-diene (H), also explains the appearance of the ethylidene-substituted compounds (LXV) (see Scheme 9).[61,63] The structures of the adducts (LXIIIa, b), (LXIVa, b), (LXVIIb), and (LXVIIIb) were established spectroscopically (NMR, CD), and also on the basis of X-ray diffraction data.[64]

The appreciable decrease in the overall yield of the cyclic photoadducts (LXIIIc) and (LXIVc), observed in the reaction of progesterone (Ic) with acetylene and pent-1-yne, and the inversion, compared with the cases examined above, of the stereospecificity of the addition, consisting in the preferential formation of ββ-isomers (LXIVc) and (LXVIIIc), are very remarkable.[62] The compounds discussed are interconverted under the influence of light λ ≥ 300 nm but are stable on irradiation with light having λ ≥ 320 nm. Since the photoaddition of both alkynes to compound (Ic) affords predominantly the 4β,5β-cyclobutenosteroids (LXIVc) and (LXVIIIc), the observed stereoselectivity is not a result of secondary reactions, but is caused, according to the authors,[62] by the influence of the acetyl group at C(17) via the mechanism of the long distance stereoelectronic effect.[65] This effect was noted for the first observation of this effect in the photochemistry of steroids.

Scheme 9

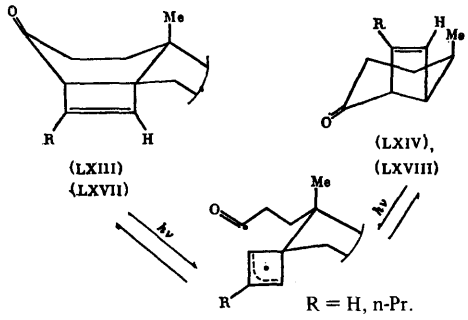


It follows from the data described that the empirical "Wiesner's rule", predicting the stereospecific course of the photoaddition of polycyclic–enones,[47] does not hold for alkynes, like "Corey's rule",[45] which predicts the structural specificity of this reaction.

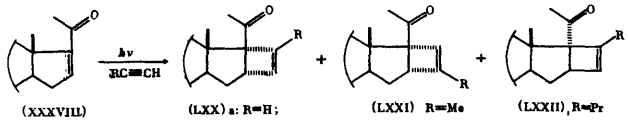
The cyclobutenosteroids (LXIIIb), (LXIVb), (LXVIIb), and (LXVIIIb) are extremely reactive compounds because of the presence of a strained double bond and the keto-group in their conformationally rigid structure. As noted above, on irradiation with light at λ ≥ 300 nm, they are interconverted via the 1,3-acyl shift mechanism, together with rapid polymerisation.[62,63]

The photoadducts considered can be converted into other steroids modified in the *A* ring. Thus, on treatment with TsOH, compound (LXVIIIb) gives rise to the bridged βγ-unsaturated ketone (LXIX) (see Scheme 9). Under analogous conditions, compound (LXIVb) does not undergo an isomerisation of this type.[62]

There exist data on the interaction of Δ^4-3-keto- and Δ^{16}-20-ketosteroids of the pregnane and corticoid series with different mono- and di-substituted actylenes.[4,66,106]



The cyclobutenosteroids (LXXa, b) and (LXXI) have been obtained by irradiating DPA [compound (XXXVIII)] in the presence of methylacetylene or acetylene.[33,103] The reaction proceeds stereospecifically from the region of the steroid molecule[67,68] and in the case of methylacetylene both regioisomers, (LXXb) and (LXXI), have been described. The interaction of DPA with pent-1-yne leads to a mixture of the stereoisomeric cyclic HH αα- and ββ-adducts (LXXc) and (LXXII) in proportions of ~10:1:[69,70]



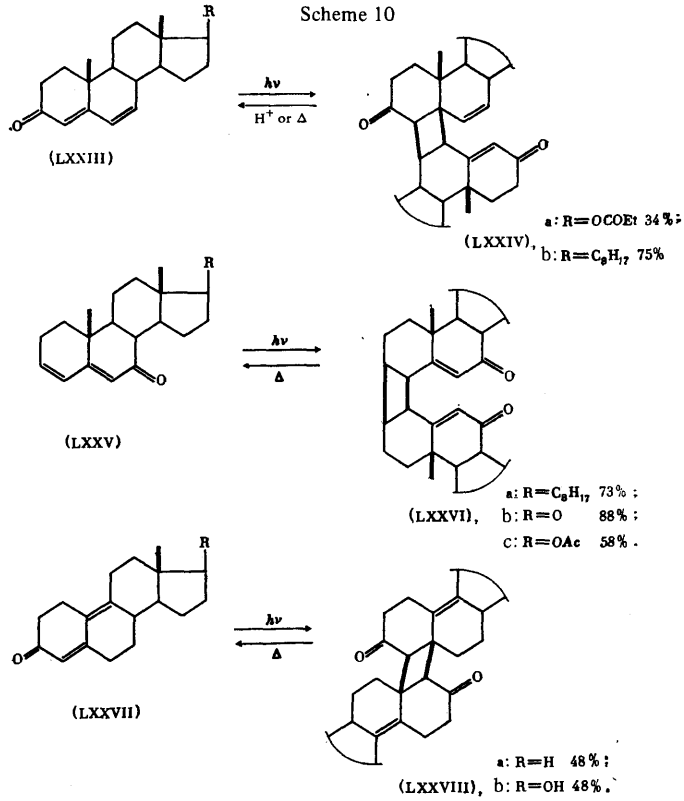
The catalytic hydrogenation of the cyclobutenosteroids (LXXa–c) leads to the corresponding cyclobutane analogues.[13,69]

IV. PHOTODIMERISATION OF STEROID DIENONES

The photodimerisation of conjugated ketones can be regarded as one of the variants of the formation of a cyclobutane ring which has found an interesting application to the steroid series. Such photodimers were first obtained and characterised by two groups of workers at the beginning of the 1960's. Thus, after irradiating the androstadienone (LXXIIIa) derivative with UV light, Rubin et al.[71] isolated as the only reaction product a dimer to which the structure of the adduct (LXXIVa) of HT type was attributed on the basis of spectroscopic data and was subsequently confirmed[72] (Scheme 10).

Analogous dimerisation has been described[73] for cholestadienone: when compound (LXXIIIb) was irradiated, the photodimer (LXXIVb) was isolated in 75% yield. Thus the dimerisation proceeds in this case via the addition of the αβ-double bond (Δ^4) in one molecule of the dienone (LXXIII) to the γδ-bond (Δ^6) of the scond monomer. The dimerisation pathway is determined by the characteristic environment of the chromophore and steric factors play a decisive role here. For example, the dimerisation of the steroid $\Delta^{3,5}$-7-ketones (LXXVa–c) afforded in all cases high yields of only one regioisomer, namely (LXXVIa–c) of the HH type,[74] i.e. the product of the addition of the γδ-double bonds of both monomeric molecules of compound (LXXV). Apparently steric hindrance prevents the approach by the second bulky molecule of compound (LXXV) to the αβ-double bond of the first monomer, whereas on irradiation of compound (LXXVa) in cyclopentene the corresponding cyclic 5,6-adduct was isolated.[74] The rate of dimerisation of compound (LXXV) is much lower than the rate of dimerisation of compound (LXXIII). The photoirradiation of the dienone (LXXVII), in the molecule of which the γδ-double bond is sterically hindered, has also been investigated. This dienone affords a lower yield of the unstable dimer (LXXVIII), than the reaction involving the Δ^4-bonds alone.[5,75] In contrast to the 17β-hydroxy-$\Delta^{4,9}$-ketone (LXXVIIb), the 17β-acetoxy-derivative forms a dimer via a reaction of the HH type.[105] On heating in the crystalline state or in solution, the dimers (LXXIV), (LXXVI), and (LXXVIII) decompose with formation of the corresponding monomeric molecules.

Scheme 10



The nature of the excited state of the steroid βγ-hexadienone systems, including their triplet π,π* state, has been investigated quantum-chemically; the results of this study do not conflict with purely chemical conclusions concerning the structure of the dimers (LXXIV) and (LXXVI).[71, 73,76] It was shown in this connection that, whereas the positive charge is concentrated on the C(3) atom of the diene component of the steroid dienone, which is in the ground state, in the π,π* state the greatest positive charge is on the C(4) atom. In view of these considerations, the formation of a bond between the C(3) atom of one molecule and the C(4) atom of a second steroid dienone appears unlikely.[76]

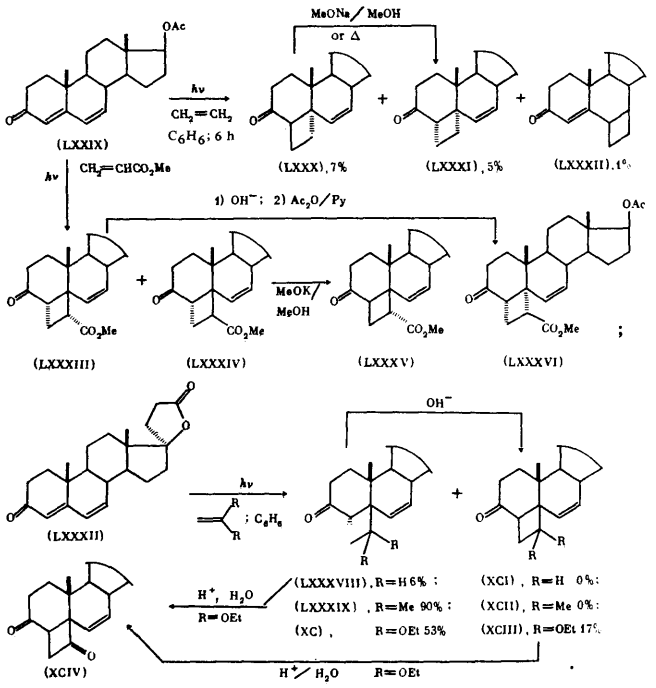
V. PHOTOCYCLOADDITION OF ALKENES TO STEROID DIENONES

The photocycloaddition of various alkenes to steroid dienones proceeds in a more complex manner than for αβ-unsaturated ketosteroids and frequently leads to a complex mixture of adducts produced via both αβ- and γδ-double bonds of the initial dienone and differing in their structures

and stereochemistry depending on the mode of addition of the alkene.

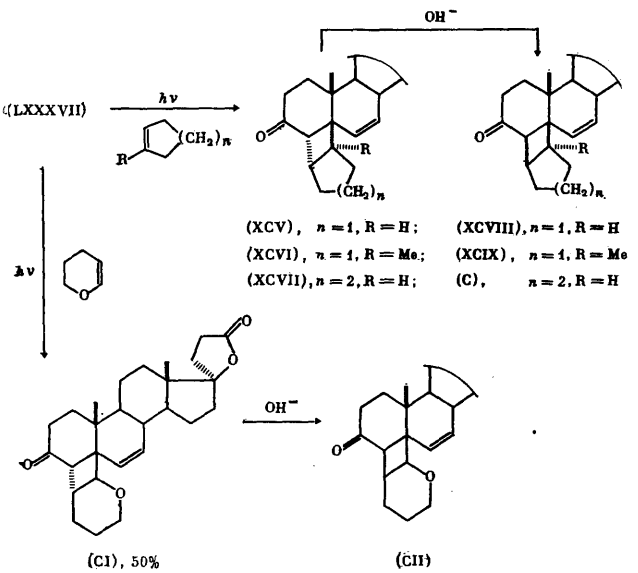
Ethylene is a relatively unreactive component of the [2 + 2]-photocycloaddition reaction. Irradiation of a benzene solution of the acetate (LXXIX) in an atmosphere of ethylene affords a low yield of *trans*-4β,5α- and *cis*-4α,5α-cyclobutanosteroids (LXXX) and (LXXXI) and also a 1% yield of the cyclic 6β,7β-adduct (LXXXII) [77] (Scheme 11):

Scheme 11



The structures attributed to compounds (LXXX)–(LXXII) are based on spectroscopic and certain chemical data. Thus *trans*-(LXXX) is known to isomerise readily to the *cis*-4α,5α-adduct (LXXXI) on treatment with sodium methoxide in methanol or thermally. The addition of ethylene to the $\Delta^{4,6}$-3-ketone (LXXXVII) has been achieved; [78] in this case the only product isolated (in 6%) yield was *trans*-4α-5β-cyclobutane (LXXXVIII), whose structure has been confirmed by data obtained by chiro-optical methods and also by the ready isomerisation to 4β,5β-cyclobutane (XCI). The photocycloaddition of a number of cyclic and acyclic alkenes to the ketone (LXXXVII) has also been investigated (see Scheme 11). The introduction of electron-donating substituents into the alkene molecule entails a sharp increase in the reaction rate and in the yield of cyclic adducts. [78] Thus isobutene adds to compound (LXXXVII) 20 times faster than ethylene and only *trans*-4α,5β-cyclobutane (LXXXIX) has been obtained in 90% yield. The addition of diethoxyethylene affords a 70% yield of a mixture of the adducts (XC) and (XCIII) in proportions of 3 : 1. The ready conversion of the *trans*-adducts into 4β,5β-isomers (XCI)–(XCIII) has been noted in all cases. The 4β,5β-cyclobutanone (XCIV) has been obtained by hydrolysing a mixture of cyclic adducts (XC) a and (XCIII). Cyclic alkenes also react with the photo-excited dienone (LXXXVII) (Scheme 12); for example, cyclopentene gives rise to only the one *trans*-adduct (XCV) in 50% yield, [38,78] while methylcyclopentene and methylcyclohexene react to form a mixture of the cyclic adducts (XCVI) and (XCIX), on the one hand, and (XCVII) and (C), on the other, respectively:

Scheme 12



The addition of dihydropyran to compound (LXXXVII) leads only to the *trans*-4α,5β-adduct (CI). All the *trans*-4α,5β-adducts (XCV)–(XCVII) and (CI) obtained readily isomerise to the *cis*-4β,5β-adducts (XCVIII)–(C) and (CII). [78]

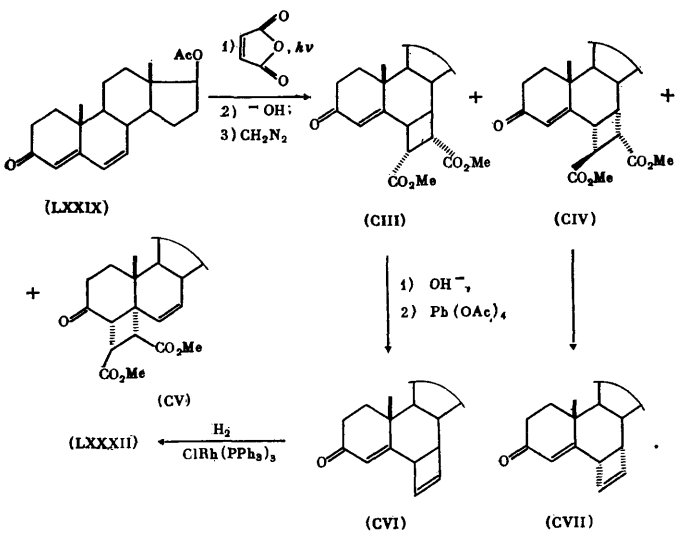
Thus the specificity of the photocycloaddition of alkenes to steroid $\Delta^{4,6}$-3-ketones, leading exclusively to *trans*-4α,5β-derivatives, has been noted in all cases.

The formation of the 4β,5β-epimer has been explained by the isomerisation of the *trans*-adduct during the photochemical reaction. Here it is assumed that, if the *cis*-adduct had in fact arisen as a result of cycloaddition, it should have had to possess the αα-structure. The stereochemical and orientational selectivity of the given reaction is explained by the fact that the dienone interacts in the excited singlet state, in contrast to the excited triplet state usually observed in photochemical cycloaddition reactions. [78]

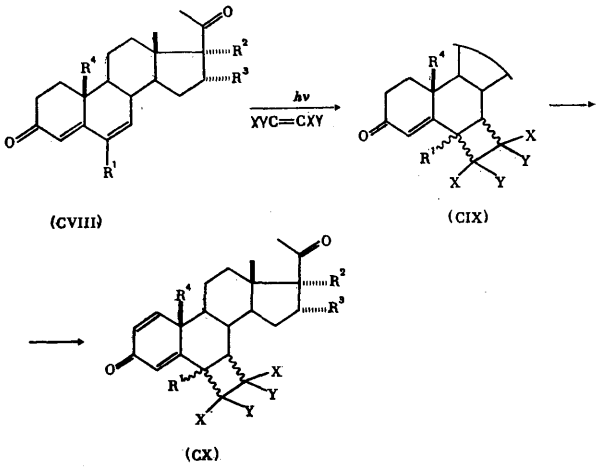
The photoaddition of methyl acrylate to Δ^{6}-testosterone acetate (LXXIX) (Scheme 11), which proceeds in accordance with the [2*s* + 2*a*] scheme, leads to the *trans*-substituted cyclobutane (LXXXIII); the epimer (LXXXIV) was also isolated in the chromatographic separation. The hydrolysis and isomerisation of compound (LXXXIV) (MeOK–MeOH) with subsequent reacetylation leads to *cis*-4β,5β-cyclobutane (LXXXV). Under analogous conditions, *trans*-(LXXXIII) was converted into the diester (LXXXVI) (the given stereochemistry was attributed on the basis of some of its chemical and chiro-optical properties). [79] The photocycloaddition of cyclopentene to the dienone (LXXIX) adsorbed on silica gel has been investigated. [43] Apart from cyclic *trans*-4α,5β-adduct of the type of (LXXXVIII), which is the sole product of the reactions carried out in methanol, the corresponding cyclic 6,7-adduct is also formed in 30% yield in this instance. We may recall the photoaddition of maleic anhydride, reacting in the excited state, to Δ^{6}-testosterone acetate (LXXIX) in the ground state [77] (Scheme 13). Here the main product is that resulting from the addition to the γγ-bond of the steroid dienone—the diester (CIII) (55%) (obtained after the methanolysis of the primary cyclic adduct) and its 6α,7α-isomer (CIV) (19%). The yield of the photoadduct (XV), formed as a result of the addition to the αβ-bond, does not exceed 15%. The *exo*-disposition of the methoxycarbonyl groups has been attributed to compounds (CIII)–(CV).

The oxidation of compounds (CIII) and (CIV) by $Pb(OAc)_4$ leads smoothly to the cyclobutenes (CVI) and (CVII). The homogeneous hydrogenation of the former in the presence of Wilkinson's complex afforded the familiar[77] cyclobutane (LXXXII):

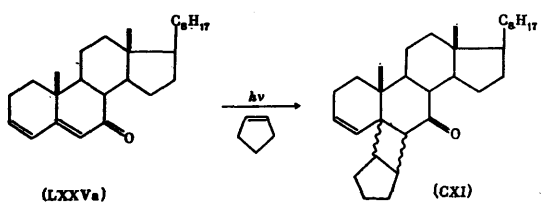
Scheme 13



A series of 6α,7α- and 6β,7β-cyclobutanopregnanes (CIX) and their 19-nor- and 17-, 16-, and 6-substituted analogues have been obtained by irradiating $\Delta^{4,6}$-3-ketopregnanes having the general formula (CVIII) in benzene in the presence of various alkenes; 4α,5α-,4β,5β-, and 4α,5β-cyclobutanes have also been mentioned as other products. The $\Delta^{1,4}$- derivatives (CX) have been obtained by chemical reactions of the cyclic adducts (CIX):[6]



The analogous 6,7-cyclobutanes of the androstane series have also been obtained.[7] The cyclic 4,5-adduct (CXI), whose stereochemistry has not been established, has been obtained by the cycloaddition of cyclopentene to cholesta-3,5-dien-7-one (LXXVa):[74]



Thus a characteristic feature of the photocyclisation considered is the ability of the steroid Δ^4- and $\Delta^{4,6}$-3-ketones in the π,π* state to form the *trans*-joined 4,5-cyclobutanosteroids, which differ significantly from the familiar results of the dark [2 + 2]cycloaddition; apparently it can be explained by the conformational flexibility of the *A* ring in the steroid systems considered (only the *cis*-adducts have been obtained for the *C* and *D* rings).

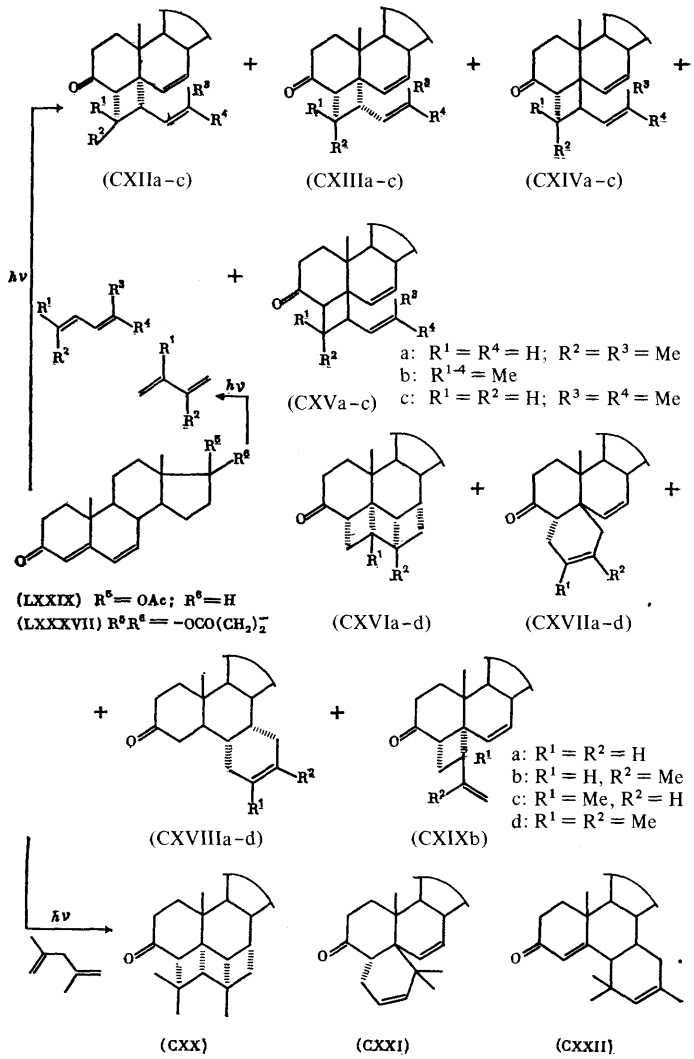
VI. PHOTOCYCLOADDITION OF DIENES TO STEROID DIENONES

It is well known that, when 1,3-dienes enter into a dark reaction with compounds containing an activated double bond, they give rise to the *cis*-products of the [2 + 2]- and [2 + 4]-cycloaddition.[80] On the other hand, the photoinduced addition of dienes leads to both *cis*- and *trans*-joined cyclic adducts. In the steroid series, this reaction has been investigated in detail by Lenz,[48,81-85] who showed that the 4,6-dien-3-ones (LXXIX) and (LXXXVII) interact with cyclic and ancyclic dienes (Table 2, Schemes 14 and 15), producing complex mixtures of substances, whose structures and stereochemistry and also composition depend on the structure of the diene and certain other factors. The results presented indicate that the isomeric cyclobutanosteroids are formed exclusively via the αβ-double bond (Δ^4-bond) of the initial steroid, which may be accounted for by its steric accessibility compared with the γδ-double bond. As can be seen from the data in Table 2, the ratio of the [2 + 2]- and [2 + 4]-adducts and the yield of the 4,5-cyclobutanosteroids depend in a definite manner on the conformation of the diene. Thus, in the reactions with transoid dienes (Table 2, compounds Nos.4–6), the yield of the isomeric cyclic 4,5-butanes (CXII)–(CXIV) is very considerable.[81,82] The 4α,5β-cyclobutanosteroids (CXIV) are converted into the 4β-epimers (CXV) in solution. On the other hand, butadiene and its 2-methyl and 2,3-dimethyl derivatives (Table 2, compound Nos.1–3) as well as *s-cis*-2,4-dimethylpenta-1,3-diene (Table 2, compound No.7) altogether fail to form cyclobutanes on reaction with steroid dienones [if one disregards the formation of compound (CXIXb) in 5% yield from isoprene]. In such cases the main reaction products are cyclic [2 + 4] adducts—the *trans*-4,5-cyclohexenosteroids (CXVII) and (CXXI) and the *cis*-6α,7α- and 6β,7β-cyclohexenosteroids (CXVIII) and (CXXII)[81-85] (Scheme 14).

Table 2. The yields of the cyclic adducts (%) in the photolysis of the dienones (LXXIX)* and (LXXVII)** in the presence of dienes.

No.	Diene	IP, eV	Yield of cyclic adducts, %					Refs.
			4α, 5α, 6α, 7α, [2+2+2+2]	*cis*-4,5 [2 + 2]	*trans*-4α, 5β [2 + 2]	*trans*-4α, 5β [2 + 4]	*cis*-6α, 7α, 6β, 7β [2 + 4]	
1	Butadiene*	9.03	25—27	—	—	33—50	8(α, β)	[81—84]
2	Isoprene*	8.76	20	5	—	40	11(α, β)	[82, 85]
3	2,3-Dimethylbutadiene*	8.89	12	—	—	48	32(α, β)	[82,84,85]
4	*trans,trans*-hexa-2,4-diene	8.19	—	45	55	—	—	[82]
5	*s-trans*-2,5-Dimethylhexa-2,4-diene**	—	—	30	25	—	—	[81]
6	4-Methylpenta-1,3-diene**	—	—	17(α, α); 44(β, β)	4.5	—	—	[81]
7	*s-cis*-2,4-Dimethylpenta-1,3-diene**	—	13	—	—	24	22(α, β)	[82—85]
8	1-Vinylcyclohexadiene**	—	—	31	—	52	12(α, α)	[82]
9	Cyclohexa-1,3-diene*	8.25	—	31(α, α)	—	14(β, α)	—	[82]

Scheme 14

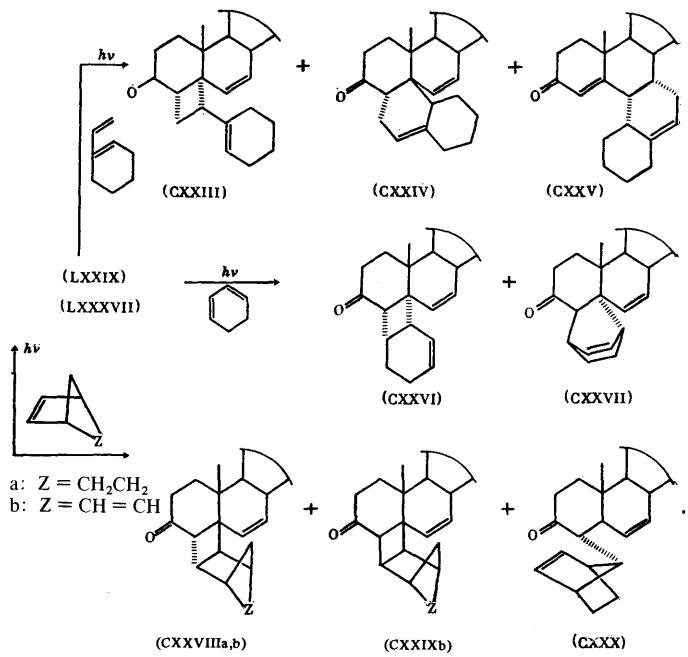


Vinylcyclohexene (Table 2, compound No.8) affords a mixture of cyclic adducts involving the Δ^4-bond: the 4α,5α-cyclobutane (CXXIII), the 4α,5β-cyclohexene derivative (CXXIV), and the product of the addition to the Δ^6-bond of the steroid dienone—compound (CXXV).[82] The interaction of the dienone with cyclohexadiene (No.9) leads exclusively to a mixture of the *cis*-4α,5α-cyclobutane (CXXVI) and the cyclic *trans*-4β,5α-adduct (CXXVII) [82] (Scheme 15).

The photocycloaddition of norbornene to the dienone (LXXXVII) leads to a 60% yield (Scheme 15) of the *trans*-4α,5β-cyclobutane derivative (CXXVIIIa), which is an exo-adduct according to X-ray diffraction data.[48] In contrast to the majority of *trans*-4α,5β-cyclobutanes, compound (CXXVIIIa) is converted into the corresponding 4β-epimer (CXXIXa) only after prolonged refluxing in methanol in the presence of sodium methoxide. Irradiation of compound (LXXXVII) in the presence of norbornadiene yielded three products: the 4α,5β- and 4β,5β-cyclobutanes (CXXVIIIb) and (CXXIXb) and the 4α-derivative (CXXX).

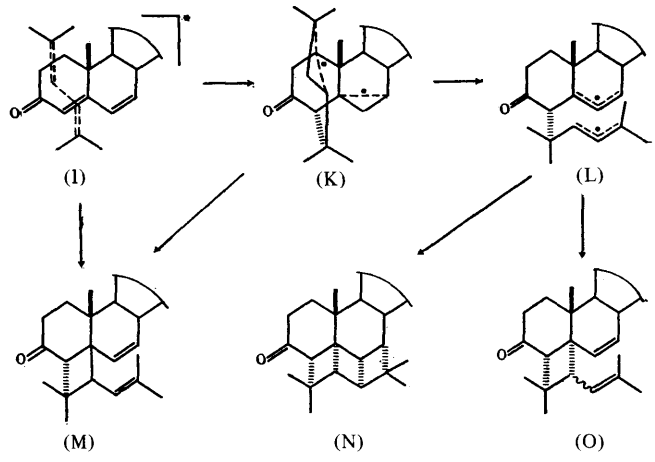
The most surprising result of the photocycloaddition of conjugated dienes to steroid dienones is the formation of "stepwise" cyclic [2 + 2 + 2 + 2]adducts (CXVI) and (CXX).[81-85] These compounds arise with a high regio- and stereo-selectivity. Thus the diene approaches exclusively the α-region of the steroid molecules, affording only a type HH adduct. Lenz[82] suggested that the possibility of the formation of the stepwise adduct depends on the ionisation potential (IP) of the diene. For IP smaller than 8.4 eV (Table 2, compound Nos.4 and 9), a product of this kind does not arise; furthermore, with increase of IP (Table 2, compound Nos.1 and 2), the yield of compound (CXVI) increases. Dienes with terminal substituents give rise to adducts of the HH type, for example, compound (CXX), while dienes with substituents at the centre of the molecule lead to a mixture of compounds (CXVIb, c).[81,82] One should also state that all the attempts to convert 4α,5α-cyclobutano-steroids (CXII) into the corresponding "stepwise" adducts were unsuccessful.[81]

Scheme 15



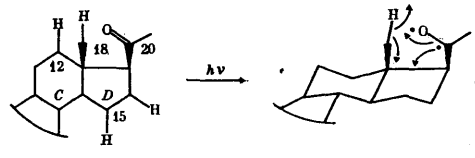
Since both the *cis*- and *trans*-cyclobutanes are formed as a result of the approach by the diene to the excited dienone in the α-region of the latter, the following reaction scheme has been proposed:[81] the photoexcited dienone interacts with the diene, to form an exciplex, in which a highly coordinating disposition of the reacting molecules obtains as a result of the adequately fixed chair conformation of the *A* ring and the presence of a pseudoequatorial current at C(4). In the complex (I), one of the double bonds of the diene is disposed orthogonally in relation to the Δ^4-bond of the dienone. Next there is a possibility of the direct formation of the *trans*-4α,5β-cyclobutanone (M), while the biradical intermediate (K) can generate, via a disrotatory transformation around the C(4α)—C bond, the allylic biradical (L), which is capable of forming the C(5)—C bond and this leads to both the *cis*-4α,5α-cyclobutane (O) and to synchronous

interaction of two allylic radicals with formation of the "stepwise" adduct (N):



VII. INTRAMOLECULAR PHOTOCYCLISATION OF STEROID KETONES

Yet another variant of the synthesis of pentaranes with an additional cyclobutane ring uses the familiar ability of carbonyl compounds to undergo intramolecular photochemical reactions with the sterically close γ-hydrogen atom (Norrish type II reactions).[86] In the series of 2-keto-steroids, such interaction is possible, in principle, with the C(12), C(15), and C(18) centres. However, the 20-carbonyl and 18-methyl groups are most favourably disposed on purely steric grounds:

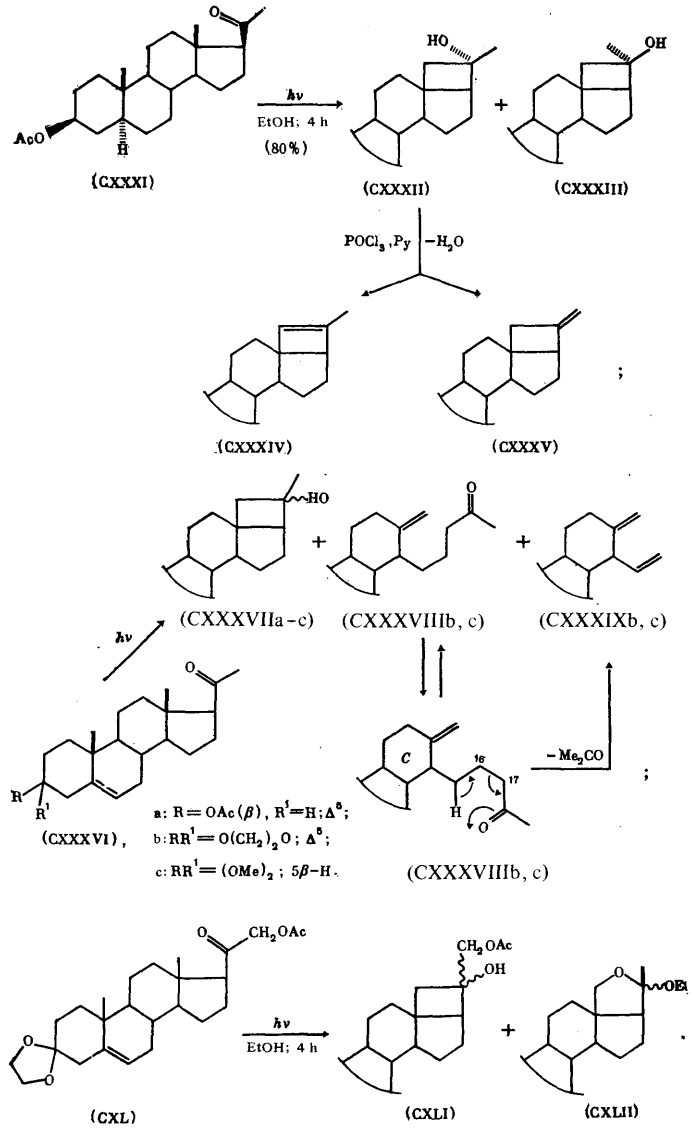


It has been shown that, when the 20-ketone (CXXXI) is irradiated in ethanol, a mixture of epimeric 13β,17β-cyclobutanols (CXXXII) and (CXXXIII) is formed in 80% yield in proportions of 3 : 1. A mixture of the alkanes (CXXXIV) and (CXXXV) was obtained by the dehydration of the 20α-epimer (CXXXII).[16,17] The structures of all these substances have been confirmed spectroscopically.[17]

The replacement of ethanol by non-polar solvents leads to the retardation of the photocyclisation and a decrease in the yield of the reaction products.[17] Thus, irradiation of compound (CXXXVIa) in hexane afforded a 33% yield of a mixture of (CXXXVIIa) epimers; compounds (CXXVIIIb, c) were obtained analogously from compounds (CXXXVIb, c) together with appreciable amounts of the D-secosteroids (CXXXVIIIb, c) and (CXXXIXb, c).[17,87] Compounds (CXXXVIII) and (CXXXIX) evidently arise as a consequence of the occurrence of two competing and consecutive photo-retro-reactions (Norrish type II), leading to the dissociation of the C(13)–C(17) bond and then the C_{16}–C_{17} bond.[17,87]

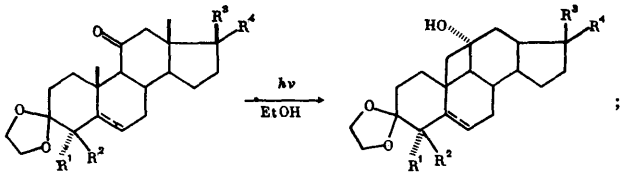
The cyclosteroids (CXXXVII) have been used as intermediates in the introduction of functional groups at the C(18) centre in the synthesis of aldosterone and its analogues.[88,89] Isolated information about such hydroxycyclobutanosteroids is available in patents.[90,91]

Substituents in the α-position relative to the 20-carbonyl group affect the course of the intramolecular photocyclisation. Thus the acetoxyketone (CXL) proved to be less active than the ketone (CXXXVIb); its irradiation leads to an equimolar mixture of the isomeric cyclobutanols (CXLI) and the tetrahydrofuran derivative (CXLII). The formation of the latter can be explained by the interaction of the excited carbonyl moiety of the 21-acetoxy-group with the 18-methyl group.



The extension of the reaction considered to the 11-keto-derivatives of steroids led to the synthesis of 11,19-cyclosteroids containing an additional four-membered ring condensed with the *B* and *C* rings.[92–96] Thus irradiation of the 11-ketones (CXLIII) in ethanol afforded 10β,11β-cyclobutanosteroids (CXLIV).[94,97,98] The yield of the latter depends to a definite extent on the presence of a substituent at C(4) and on the character of the junction of the *A* and *B* rings and is a maximum for the 4,4-disubstituted *A*–*B*-*cis*-compounds, because cyclisation in such steroids eliminates the steric interaction between the 4β-CH_3 and the 19-CH_3

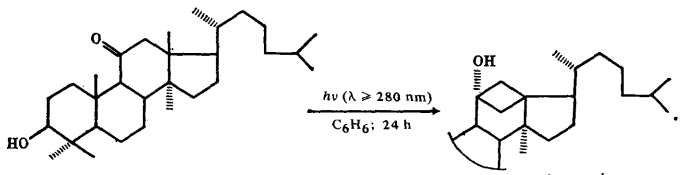
groups in compound (CXLIII):



(CXLIII) (CXLIV)

R^1 and R^2=H, Me; R^3, R^4=$O(CH_2)_2O$ or R^3=C_8H_{17}; R^4=H.

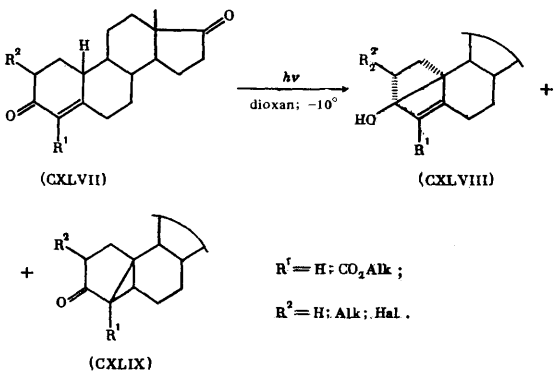
The character of the junction of the *C* and *D* rings and also the presence of the 14α-CH_3 group in the initial 11-keto-steroid affects the photocyclisation under consideration. Thus the Δ^{14}-11-ketosteroids form on irradiation the 11,8-cyclopropane derivatives;[99] the 11-ketone of the lanostane series (CXLV) is converted in ~20 yield into the 11β,13β-cyclobutanol (CXLVI):[100,101]



(CXLV) (CXLVI)

The cyclic 11,19-photoproducts in the series of triterpenoids have also been described.[92,93,102] It is noteworthy that the 11-keto-C-norsteroids do not undergo intramolecular cyclisation.[95]

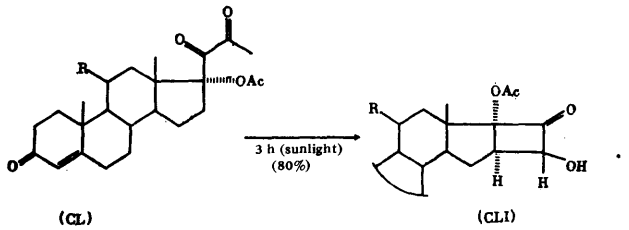
The 19-nor-Δ^4-3-ketosteroids substituted in the *A* ring produce on irradiation a low yield of the 3,10-cyclobutanol compounds (CXLVIII) together with the 4,10-cyclopropane derivatives (CXLIX):[104]



(CXLVII) (CXLVIII)

(CXLIX)

The 16,17-cyclobutanosteroid (CLI), obtained in a high yield on irradiation of compound (CL) with sunlight, has also been described:[19]



(CL) (CLI)

---oOo---

Thus the review of the literature data on the synthesis of cyclobutanosteroids (pentaranes) by photochemical methods shows that the main process in the photochemical [2 + 2]addition of unsaturated substrates to the active double bonds in the steroid molecule is sometimes accompanied by the simultaneous reactions involving both the initial steroid and the primary cyclic adducts.

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Mechanochemical Synthesis

C.Simionescu and C.V.Oprea

The mechanism and conditions in the mechanodegradation of certain homochain and heterochain polymers as well as mechanochemical graft and block copolymerisation, polycondensation, and mechanochemical complex formation processes are examined. These yield a virtually complete description of the behaviour of test polymers in mechanochemical processes; the possibility of altering the structure and properties of the initial polymers in the required direction is also discussed. Attention has been concentrated on homopolymerisation and copolymerisation reactions; it is shown that the reaction mechanisms and the structures of the polymers formed possess features determined by the nature of the activating influence (mechanical energy).
The bibliography includes 129 references.

CONTENTS

I. Activation of solids, including polymers, by mechanical energy 283
II. Reactions initiated by active fragments obtained by the mechanodegradation of polymers 289
III. Reactions initiated on inorganic mechanoactivated surfaces 293

I. ACTIVATION OF SOLIDS, INCLUDING POLYMERS, BY MECHANICAL ENERGY

1. Essential Features of the Process

Mechanochemistry is a science developing at the boundary between chemistry and mechanics: it is closely related also to other branches of science and engineering—physics, especially solid state physics, biophysics, physical chemistry, polymer technology, the chemistry and technology of inorganic substances, biochemistry, molecular biology, and bionics.

By selecting and reworking certain facts and laws taken from all these branches of science, mechanochemistry has in its turn put forward its own laws and conclusions, promoting the development and enrichment of the sciences related to it.

In the most general definition, mechanochemistry can be referred to as the science which deals with the study of the interconversions of mechanical and chemical energy in material bodies.[1-3] However, the creation of a single all-embracing hypothesis reflecting comprehensively all the aspects of the mechanochemical process must be based on the knowledge of the complex structure of the test object, which is determined by a number of levels of supermolecular organisation. The mechanochemical phenomenon includes two main components: the mechanochemical component, which determines the conversion of mechanical energy into chemical energy, and the chemomechanical component, which represents the liberation of mechanical energy as a consequence of chemical reactions.

Here one must bear in mind that it is extremely difficult to tell whether the mechanical action is the primary factor inducing the chemical reaction or whether it is merely an agent facilitating the action by the medium. The field of mechanical forces influences the probability of the initiation of various reactions and the latter in their turn determine the spatial disposition of the structural elements[4] (Fig.1).

The chemomechanical aspect of the phenomenon has been discovered as a result of studies by Kuhn[5] and Katchalsky[6] using artificial systems. Similar studies have been carried out also by other investigators.[8,9] These studies are of interest not only because of their current practical value but also because they model important biological phenomena such as the transport of matter through membranes or the contraction of muscle tissue, whose mechanisms have now been virtually demonstrated.[10-23] Different variants of the "mechanochemical machine" have been published, in which the LiBr and NaCl electrolyte concentration gradients and the pH values excite the expansion and contraction of protein (collagen) or cellulose fibres, which are thus able to set in mechanical motion a system of wheels in accordance with the transmission belt principle.[7]

The most complex process responsible for the liberation of mechanical energy in living organisms is the biomechanical process, which is cyclic in character. In muscle contractions, it takes place at the level of supermolecularly organised protein macromolecules, constituting macroscopic systems, which are excited mechanically by the work of the preceeding cycle. In this state, they become the site where chemical reactions (especially of the enzyme type) take place with the biological medium. Thus an isobaric and isometric mechanochemical transformation occurs (Fig.2). Its direct result is a change in the relative disposition of atoms and groups of atoms and also a change in the conformation of the macromolecules. The conformational changes occurring at the level of each macromolecule are manifested in contraction and expansion effects at the level of the supermolecular formation incorporating these macromolecules; as a result, this formation begins to perform mechanical work. The chemomechanical transformation in the cycle (2) is thus performed (Fig.2). The mechanical energy liberated acts on the supermolecularly organised macromolecules and the latter pass to a mechanically excited state and the biomechanical cycle is repeated.[23]

Consequently the mechanochemical process combines both the transformation of chemical energy into mechanical energy and of mechanical energy into chemical energy; the site where these transformations take place is the structure subjected to the given action. The mechanochemical and biochemical processes are now known and many aspects have been investigated; these processes have found important applications in life and engineering[1,2,23-28] (Fig.3).

2. The Step-wise and Activated Character of the Mechanical Process

The step-wise character of the mechanochemical process is manifested when it is considered at different levels of the supermolecular organisation. It is determined by the structural features of the polymer, which determine the specific character of the concentration of mechanical energy in specific chemical bonds located in the zone of defects with a statistical distribution at molecular, supermolecular-morphological, and structural-composition levels.

The micromechanics of the dissociation of chemical bonds can be studied successfully using the oriented polymer model of the greatest mechanical resistance to rupture (having the profile of fibre) or on a single crystal obtained by solid-phase polymerisation.[29] Such structures possess discrete formations, clearly separated in space, with a supermolecular organisation, whose transformation induced by the mechanical action can be estimated with the aid of the usual research methods. The mechanical model of such a structure can be represented as a set of macromolecules maintained in the longitudinal direction by dispersion forces, whose nature depends on the actual chemical structure of the polymer investigated (Fig. 4*a*).

For a correct separation of the phenomena occurring in the volume element under the influence of mechanical energy, account must be taken of the following factors. Real polymers (and material bodies in general) are characterised by a structural inhomogeneity, as a result of which the distribution of mechanical stresses is non-uniform. Since the determination of the magnitude of the stresses in chemical bonds is extremely difficult, one usually determines the variation of the rate constant for the dissociation of overstressed chemical bonds. It is then necessary to know the nature of the factors influencing the probability of the onset of chain mechanodegradation and the nature of the radical reactions initiated in this way.

Simplifying conditions, consisting, for example, of assuming that the stresses are distributed uniformly over each structural and chemical bond element, are usually resorted to in the calculations. For an analytical investigation of the phenomena occurring in a volume element (Fig. 4*a*), an isolated macromolecule, having the flat zigzag shape (Fig. 4*b*) characteristic of the majority of known polymers, is considered. As a result of the action of the stretching force P_1 on this macromolecule, the valence angles and chemical bonds are deformed. According to the condition adopted, the force is distributed in equal parts P_i which act on the

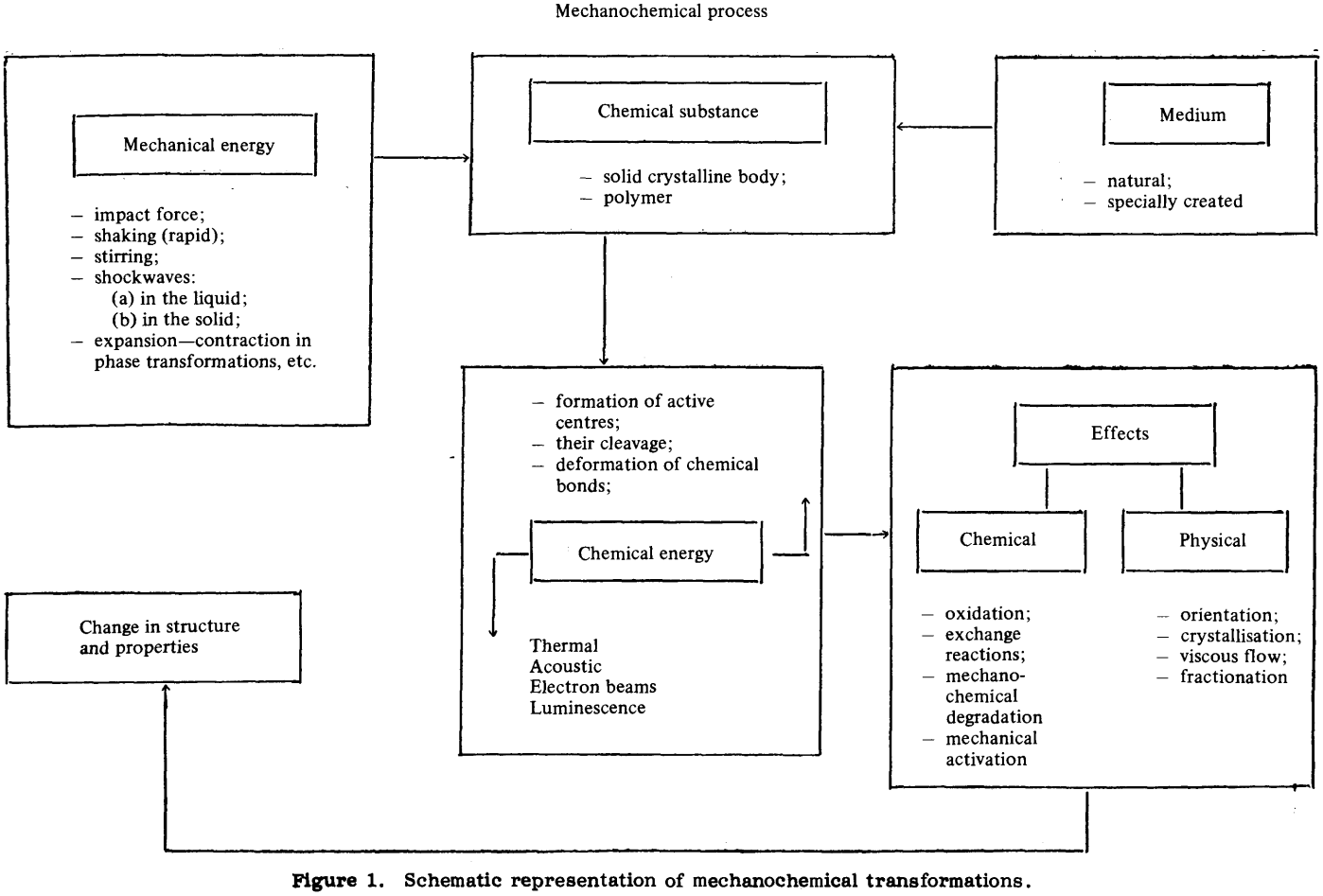


Figure 1. Schematic representation of mechanochemical transformations.

corresponding structural microelements consisting of not less than two chemical bonds (*1–2* and *2–3*) and a valence angle (*1–2–3*) (Fig. 4c) and can be divided into tangential ($P_{i,t}$) and normal ($P_{i,n}$) components. Despite the fact that the deformation of the valence angle is greater, the rupture takes place in the chemical bond. According to Natarajan and Reed,[39] we have

$$P_{t,\max} = \frac{P_{i,t,\max}}{\sin \rho_0} ,$$

where $P_{i,\max}$ is the force causing the dissociation of the chemical bond, $P_{i,t,\max}$ the tangential component at the instant of rupture balancing the resistance of the chemical bond, and ρ_0 the valence angle at the instant of rupture.

The break in the section *BC* (Fig. 4a) occurs when the latter is acted upon by a force which is determined by the length of the macromolecule with the maximum molecular weight ($P_{i,t,\max} = \Sigma n P_{i,t}$). Consequently, the chain length, expressed in terms of the number of component chemical bonds, is important for the occurrence of the rupture process. When the volume element contains macromolecules of critical length (which is much greater than the average length), its stability no longer depends on the energy of the interchain bonds but does depend on the chain length. For the critical chain lengths, the force developed is a maximum and causes the breaking of the chain, i.e. mechanocracking.

The breaking of the chains via mechanocracking is a chemical reaction but of a kind such that the participating kinetic and structural elements are not individual macromolecules but volume elements involved in the rupture. Therefore, despite the fact that the rupture occurs as a result of changes in the bonds at the atomic-molecular level, the mechanical process belongs, in essence, to the supermolecular level.

If the mass of the rupture volume element is denoted by X_2, then, after the absorption of a definite amount of mechanical energy Ω, the volume element is separated into two parts (X):[30]

$$X_2 + \Omega \rightarrow 2X .$$

The absorption of elastic energy leads to a bond dissociation volume element which is non-uniform in different regions. In those microvolumes where the potential energy becomes sufficient to overcome the energy barrier to the transition to the new state, an elementary breaking step, consisting in the transformation of the initial configuration state into another (final) state, takes place. At an intermediate stage, a configuration critical for the given conditions (corresponding to the maximum area under the potential energy curve) is attained, representing an unstable mechanoexcited complex. This complex is stabilised by the excess energy obtained by dissociation of a certain additional number of chemical bonds. The energy accumulated is then distributed among the vibrational and rotational degrees of freedom in accordance with

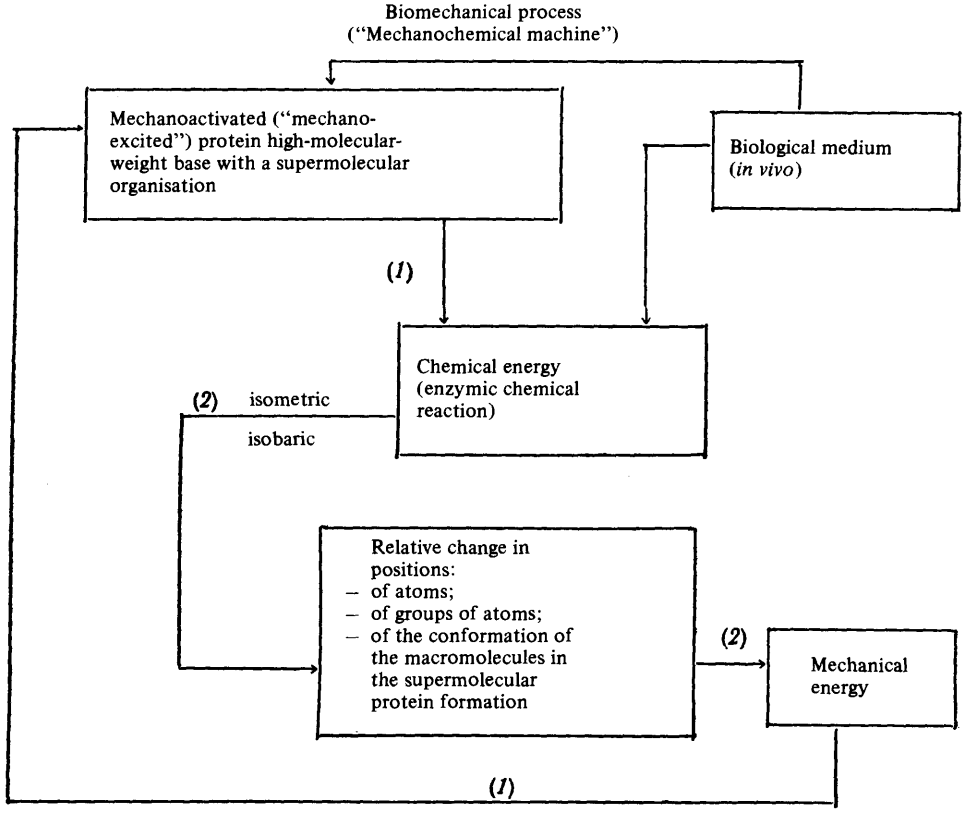
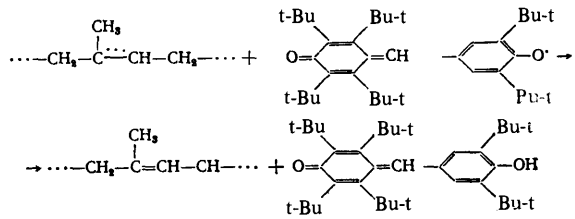


Figure 2. Schematic representation of a biomechanical process: 1) mechanochemical transformation; 2) chemomechanical transformation.

the requirements of the new configurations. Hence it follows that, in the bond deformation stage before rupture, the reactivity of the system increases with formation of mechano-excited states and free radicals, which arise as a consequence of the mechanocracking of the chemical bonds, occurring to a limited extent in the interior of the most activated micro-regions. The set of macroradicals, formed by a certain number of molecular breaks in the mechanoexcited micro-volume, leads to the appearance of an incipient microcrack.

The appearance of a mechanoexcited state and the formation of free radicals have been demonstrated by EPR studies and have been confirmed by the character of certain chemical reactions. For example, raw rubber deformed by stretching is oxidised more readily;[31–33] vulcanised rubber is ruptured more readily on exposure to ozone;[34] certain heterochain polymers are hydrolysed in the cold under the conditions of mechanical action, whilst under the usual conditions this process can occur only at elevated temperatures.[35,36] The mechanoexcited state in raw rubber enables the latter to react with stable radicals of the galvinoxyl type[37] in accordance with the scheme



When certain polyoxoamides are stretched in an inert medium in the cold, free radicals are obtained whose formation may be followed visually since they are coloured red. After the removal of the force, the active centres vanish and so does the colour, but the test specimens become insoluble in *m*-cresol.[38] The stretching of vulcanised rubber without additives at low temperatures (93–193 K) takes place with the appearance, before the onset of rupture, of fine gas

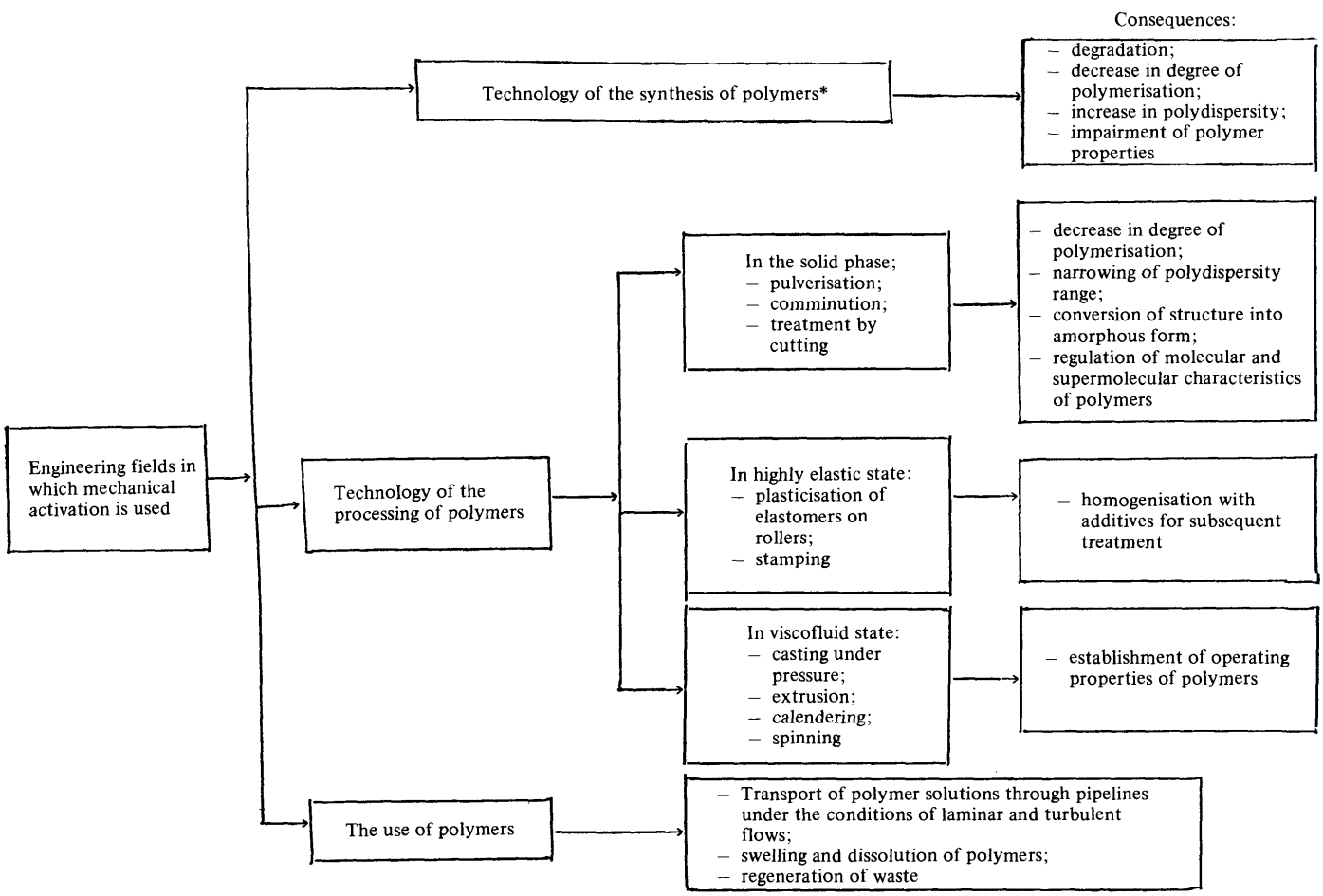


Figure 3. Technical applications of mechanochemical processes.

*Limited under the conditions of vigorous stirring of very viscous media.

bubbles on the surface of the specimens (the "foaming effect"), the gas being shown by chromatographic analysis to be hydrogen evolved on mechanical rupture of the chains. The stretching of the specimens at 93 K with the simultaneous recording of EPR spectra indicates the formation of free radicals. The amount of hydrogen evolved and the concentration of the radicals are correlated with the degree of structure formation in the elastomer and with the applied force (Fig.5 and Table 1).

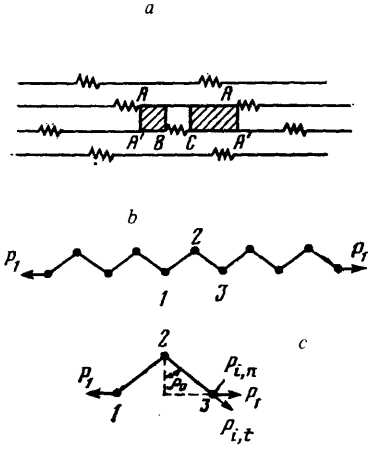


Figure 4. *a*) Mechanical model of a partly oriented polymer;[39] *b*) macromolecules subjected to the action of a force P_1; *c*) microelement subjected to the action of a force P_i.

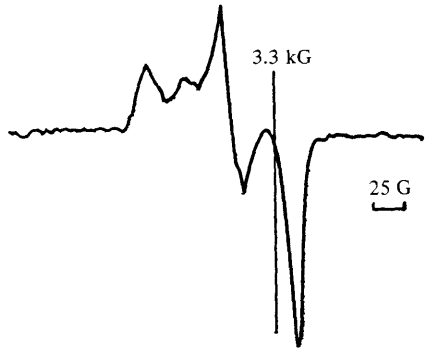
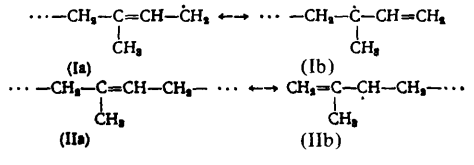
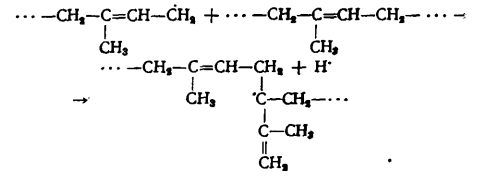


Figure 5. EPR spectrum, recorded at 200 K, of polyisoprene rubber stretched at 366 K.[39]

The results obtained show that the mechanical rupture of the chains takes place with participation of radicals in accordance with the scheme



and confirms the following mechanism:



The increase in the reactivity of the system at the deformation stage before rupture can be accounted for by the appearance of mechanoexcited states and free radicals and is defined by the term "mechanoactivation".

Table 1. Characteristics of polyisoprene rubber specimens stretched at 93 K.[39]

S, %	M_c	M_c^*	$10^{-17}a$, spins g^{-1}	l, cm^3 g^{-1}
1	11 158	10 668	4.0	28
2.5	6 082	5 370	8.9	47
4	4 385	3 850	9.5	50
6	3 364	2 934	11.1	60

Notation: M_C is the initial number-average molecular weight, M_C^* the molecular weight after the evolution of hydrogen, a the concentration of spins before rupture, l the amount of hydrogen evolved, and S the relative elongation of the specimen.

The accumulation of an increasing number of rupture volume elements generates a state promoting degradation; the free energy of the system then increases. For sufficiently high chemical potentials, the mechanochemical phenomena acquire quantitative characteristics to which corresponds the acceleration of all the chemical reactions possible in the given system by factors of tens.[40] The second step in the mechanochemical process, namely mechanocracking, takes place mainly via a radical chain mechanism at the atomic-molecular level. It results in the accumulation of degradation products with the minimum molecular weight (which is determined by the nature of the polymer and the medium, the parameters of the mechanical regime, and temperature), called the degradation limit ($\bar{M}_\infty$). The set of mechanocracking acts inducing the loss of functional properties by the polymer determines the mechanodegradation process.

The third step in the mechanochemical process proceeds mainly at the supermolecular level and consists in the reorganisation of the entire structure of the chain mechanism. This step consists of the following phases: (1) initiation occurring simultaneously with formation of incipient microcracks; this process begins already in the mechanoactivation stage (*A*, *B*, and *C* in Fig.6); (2) the growth of microcracks with formation of macrocracks from the latter (*E*); (3) the conversion of the macrocracks into the main crack capable, by virtue of its size, of generating, at its apex, stresses sufficient for the rupture of the structural element with formation of a new surface (*F* in Fig.6). At the macroscopic level, the specimen is ruptured. The rate of growth of the main cracks in the polymer v is expressed by the equation[41-44]

$$v = C \cdot \exp \frac{U_0 - \alpha\sigma}{RT} ,$$

where $c \cong 10^{10}$ cm s^{-1} is a constant, U_0 the activation energy for the growth of the main crack, α a coefficient taking into account the stresses appearing at the apex of the crack, σ the external load, R the gas constant, and T the temperature (K) at which the process takes place. The quantity U_0 is numerically equal to the activation energy for the dissociation of chemical bonds. At the instant of rupture, numerous active centres of the radical type appear as a result of the homolytic dissociation of macromolecular chains in the path of the main crack. After their stabilisation, new functional end groups are obtained, as is indicated by IR spectroscopic data.[45] The determination of the number of end groups on the surface of the main crack yielded 0.5×10^{22} cm^{-3}, which is approximately equal to the total number of chemical bonds in one cubic centimeter; consequently the surface of the main crack contains virtually only the ends of the chains.[48]

Both the incipient microcracks, which are active dynamic nuclei, and the main cracks are formed via the same mechanism, which consists in essence in the thermofluctuation rupture of chemical bonds activated by the stresses induced by the mechanical force applied from the outside.[41–47] The formation, growth, and spreading of the cracks via the mechanism indicated above are influenced signficantly by the presence of chemical agents penetrating into the depth of these cracks and accelerating the phenomena activated by the action of the force.

Consequently under the conditions of the stripping and fragmentation of the supermolecular and morphological formations in a solid polymer, the mechanical energy is consumed on the dissociation of interatomic bonds with formation of free radicals and also on the dissociation of ionic bonds (with the appearance of an electrical double layer), which can lead to the formation of new functional groups. Continuously renewed highly activated surfaces, constituting the basis for the initiation of numerous chemical reactions, are thus produced. The chemical reactions can be initiated either in the radical stage of the formation and growth of the cracks or later. The occurrence of these reactions is facilitated by the appearance of new functional groups and by the loosening of the structure of the specimen, which increases the accessibility of the active centres to chemical agents.

3. The Nature of the Primary Active Centres

Analysis of the elementary act in a mechanochemical process should have as its starting point the determination of the nature of the primary active centre appearing on decomposition of the mechanoexcited state.

The molecular transitions from the ground state to the activated state take place from a bonding orbital (π or σ electron) or from a non-bonding orbital (p electron) to an antibonding orbital (π^* or σ^* electron), which disturbs the distribution of the bulk of electron density. This tends to destabilise the chemical bond in the polymer.[47] The energy corresponding to excited states greatly exceeds the strength of any >C–C< chemical bond (Table 2), so that the recombination of the macroradicals generates insufficient energy to excite the neighbouring species (macromolecules, radicals).

Table 2. Electronic transitions for certain polymers (specimens in the form of films).

Polymer	λ_{max}, nm	$h\nu_{max}$, kJ mol^{-1}	Transition
Polyethylene	150	802	$\sigma \rightarrow \sigma^*$
Polybutadiene	180	670	$\pi \rightarrow \pi^*$
Polystyrene	187—200	461—645	[a]
Poly(methyl methacrylate)	214	561	$p \rightarrow \pi^*$
Poly(ethylene terephthalate)	290	415	$p \rightarrow \pi^*$
Poly(ethylene terephthalate)	240	502	[a]

[a] Taking into account the π-electron system.

For the idealised case of the dissociation *in vacuo* of chemical bonds of different types ranging from homopolar to purely ionic, two variants of such dissociation can be put forward:

$$\cdots\text{—}R_1\text{—}R_2\text{—}\cdots \longrightarrow \begin{cases} \cdots\text{—}\dot{R}_1 + \dot{R}_2\text{—}\cdots, \\ \cdots\text{—}\overset{(+)}{R}_1 + \overset{(-)}{R}_2\text{—}\cdots. \end{cases}$$

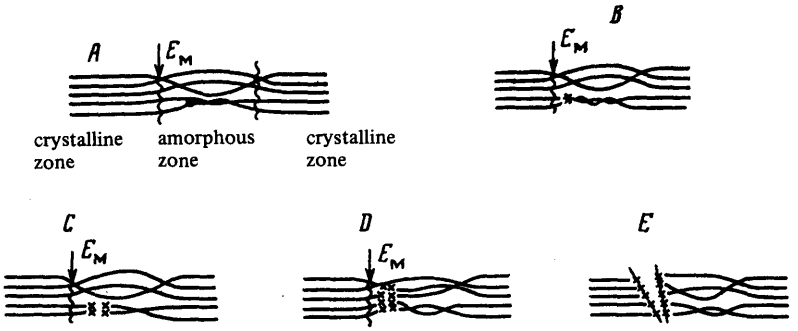


Figure 6. Stages of the mechanochemical process in the degradation of polymers (the arrow indicates the site where the mechanical energy E_m is concentrated—the junction of the crystalline and amorphous zones; the filled circle denotes a structural defect in the amorphous zone; the star denotes a structural defect mechanoactivated by the stress due to the action of mechanical energy E_m).

Positive ions or radical-ion centres with an energy level below that of the excited state appear with the greatest probability. Since the dissociation of $\ldots-R_1-R_2-\ldots$ into molecular ions requires an additional energy equal to 672 kJ mol^{-1} or even more, the above dissociation is more economical from the energetic standpoint than the homolytic dissociation.

After the formation of free radicals, the carbon–carbon bonds located in the α-position relative to the carbon atom with the unpaired electron proved to be to some extent stronger than in the ground state, while the bonds in the β-position are weaker. The subsequent rupture of the hydrocarbon chain containing the radical involves the formation of a double bond and the liberation of energy (250–280 kJ mol^{-1}). This shows that the activation energy is smaller for reactions of this type (Table 3).[47]

Table 3. The activation energies E_a for the rupture of chains containing a radical.[47]

Polymer	E_a, kJ mol^{-1}	Polymer	E_a, kJ mol^{-1}
Polyethylene	118	Poly(vinyl fluoride)	116
Polypropylene	102	Poly(vinylidene fluoride)	131
Polyisobutylene	76	Polytetrafluoroethylene	147
Polystyrene	85	Poly(vinyl acetate)	118
Poly(α-methylstyrene)	95	Poly(methylmethacrylate)	98
Poly(vinyl fluoride)	87	Poly(methyl acrylate)	85
		Polycaprolactam	117

The activation energies for the dissociation of bonds at the atom with the unpaired electron have been calculated by Kagya et al.[48] Free radicals are obtained as a result of the dissociation of chemical bonds not only in organic but also in organoelemental or inorganic polymers. The mechanical dispersion of quartz leads to the liberation of active species,[49–51] whose paramagnetic character has been demonstrated chemically or with the aid of paramagnetic nuclear resonance.[52–54] On mechanical dispersion of $SO_2/BaSO_4$, electrons in the form of *F* or *Y* centres were discovered not only at low temperatures.[2,27] An electrical double layer is formed via the dissociation of adhesion bonds on newly formed surfaces in contact, which generates a very intense electric field. The electrons leaving their initial positions move away from the newly formed surfaces into the bulk of the body, which leads to its electroexcitation. The electrical discharges induced by the activation of solid surfaces in contact and also of the newly formed surfaces liberate electrons which are capable of participating in subsequent mechanochemical reactions.[27]

II. REACTIONS INITIATED BY ACTIVE FRAGMENTS OBTAINED BY THE MECHANODEGRADATION OF POLYMERS

Studies on graft block copolymerisation have been undertaken because of the need to devise processes permitting the synthesis of compounds with the necessary predetermined properties. The aim of such research has been to obtain copolymers whose components would arise from significantly different polymers (natural and synthetic, polar, highly elastic, and rigid), so that the resulting compounds should combine the properties of the initial components.[55–59]

The mechanical activation of graft block copolymerisation is thought to be one of the most economically efficient ways of obtaining new products using the equipment generally adopted for the treatment of the initial polymers. Mechanical grafting was used initially to elucidate the character of the mechanism of the mechanochemical degradation of polymers[1,2,60–64] and only later as a method for the specific transformation of their structures and properties for practical purposes.[65–73]

1. Mechanical Grafting in a Polymer–Monomer System

The initiation of chemical reactions in a polymer–monomer system is due to the presence of radicals formed on cleavage of the polymer macromolecules subjected to mechanical treatment. In principle, the active primary centres should induce the formation of block copolymers in the presence of monomers. However, in practice, the simultaneous occurrence of graft polymerisation is observed, since chain transfer and in certain cases also cross-linking are unavoidable under the conditions of a radical mechanism. At the present time there are no methods which would make it possible to establish their specific contribution to the formation of the final product.

Table 4 presents only a few examples of the numerous systems investigated, which have a bearing on the specific alteration of certain properties of the polymer base. For example, non-polar polymers alter the character of the structure formation processes after grafting with the aid of acrylic acid, maleic anhydride, or a mixture of the above compounds to styrene, vinyl acetate, acrylonitrile, or methyl methacrylate.[68–72]

The improvement of surface-active properties has been achieved by grafting polar monomers to certain polymers of the polyamide[65] or polyester[66,67] type, which made it possible to overcome one of the main disadvantages of synthetic fibres—the lack of exchange of moisture with the external medium. Norbornene and SO_2 polymerise rapidly in the presence of mechanoradicals† formed, for example, from polyisobutene subjected to rapid stirring in solution. This reaction has been recommended as a method for the recognition of free radicals.[72]

2. Mechanochemical Grafting–Block Copolymerisation in a Polymer–Polymer System

A mixture of polymers has been most frequently jointly subjected to a treatment in order to improve technological and operating properties. In many cases the process conditions were the same as those usually employed in technological treatment and in some cases industrial equipment has been used.

In principle, the synthesis is initiated by the usual active fragments obtained by the rupture of macromolecules acted upon simultaneously by mechanical and thermal factors. The reactions of the active centres formed are as a rule subsequently complicated owing to mechano- and thermo-oxidative effects, which are unavoidable when the reaction takes place in the presence of atmospheric oxygen. By acting as a universal radical acceptor, atmospheric oxygen usually accelerates energetically initiated processes.

† Here and henceforth in the review the term mechanoradicals will be applied to radicals formed on mechanoexcitation.

Table 4. Graft block copolymers synthesised in a polymer–monomer system.

Polymer base	Type of active centre		Monomer	Conditions of treatment	Mechano-chemical reaction	Result	Refs.
	1	2					
Poly(ε-caprolactam	NH–CO–$\dot{C}H_2$ *	...–NH–CO–$\dot{C}$H–	Styrene	Vibromilling inert medium; $T = 18 \pm 2$ °C	Graft block copolymerisation	—	[65]
Polyhexamethyleneadipamide	Ditto	Ditto	Vinyl chloride	Ditto	Ditto	—	[65]
Ditto	»	»	Acrylonitrile	»	»	—	[65]
»	»	»	Acrylic acid	Vibromilling, inert medium; T = 196 °C	»	Surfactants	[66]
Poly(ethylene terephthalate)	...–C(=O)–O$\dot{}$ + + $\dot{C}H_2$–CH_2–...	...–C(=O)–O–$\dot{C}$H–...	Vinyl chloride, acrylonitrile, vinyl acetate	Vibromilling, inert medium; $T = 18 \pm 2$ °C	»	Hydrophilic properties	[67–81]
Ditto	Ditto	...–C(=O)–OCH_2–$\dot{C}$H–...	Ditto	Ditto	»	Ditto	[67–81]
»	»	Ditto	Acrylic acid	Cryolysis (freezing/thawing cycle); $T = -40$ °C	»	»	[67–81]
»	»	...–C(=O)–O–$\dot{C}$H–...	Ditto	Ditto	»	»	[67–81]
Poly(1,4-*cis*-isoprene), synthetic and natural	...–CH_2–CH=C(–CH_3)–$\dot{C}H_2$	...–$\dot{C}$H–CH=C(–CH_3)–CH_2–	Maleic anhydride	Plasticisation; room temp.	Graft block copolymerisation	Regulates gel formation	[69,70]
Ditto	Ditto	...–CH_2–CH=C(–$CH_2$$\dot{O}$)–$CH_2$	Maleic anhydride jointly with styrene, methacrylate, vinyl acetate, and acrylonitrile	Ditto	Ditto	Ditto	[69,70]
Polyisoprene, natural	...–CH_2–CH=C(–$\dot{C}H_2$)–CH_2	...–CH_2–CH(R)–$\dot{C}$(–CH_2)–... **	Styrene	Plasticisation on rollers	Graft block copolymerisation	—	[71]
Polyisobutylene	CH_3 | ...–CH_2–$\dot{C}$ | CH_3	—	Norbornene + SO_2	Rapid stirring; room temp.	Block copolymerisation	—	[72]
Polytetrafluoroethylene	F | ...–CH_2–$\dot{C}$ | F	CH_2 | ...–CH_2–$\dot{C}$ | C=O | OCH_3	Methylmethacrylate	Vibromilling, inert medium; T = 77 K	Grafting	Hydrophilic properties	[73]
Ditto	Ditto	H | ...–$\dot{C}$–CH_2 | $OCOCH_3$	Ditto	Ditto	Block copolymerisation	Ditto	[73]
»	»	Ditto	Ethylene	»	Ditto	»	[73]

*The radicals were determined by EPR.

**$R^{\cdot} = -CH_2-\dot{C}(CH_3)=CH_2$.

Table 5 presents a series of examples of the synthesis and properties of such products. The treatment of polyethylene (PE) and polypropylene (PP) was carried out both in the presence of certain polar rigid-chain polymers, such as, for example, ethylcelluloses (EC) or ε-polycaprolactam (PC),[74–75,80,81] and certain elastomers.[77–79] The PE/EC system was subjected to a thermomechanical action on a Bradenberg plastograph. It was then shown that the decisive factors in the formation of active centres are the component ratios, process time, and temperatures, while the occurrence of the process itself is influenced significantly by the presence of oxygen, which accelerates the primary radical reactions and leads to cross-linking (Fig.7).[74,75] The PE/PC system was treated by vibromilling at low temperatures

Table 5. Graft block copolymers synthesised in a polymer–polymer system.

Polymer base	Modifying agent	Conditions of treatment	Mechanochemical reaction	Result	Refs.
Polyethylene, low density	Ethylcellulose	Plasticisation on Brabender plastograph; $T = 165$ °C; in air	Graft block copolymerisation; structure formation	The polymer base becomes insoluble; calculation of the fluidity coefficient of the melt; improvement of dielectric properties	[74]
Ditto	Poly(ε-caprolactam)	Vibromilling in an inert medium; $T = 0$–-40 °C	Ditto	Increase in hydrophilicity	[75]
Polyethylene, high density	Polyisobutylene	Extrusion; $T = 150$–260 °C	Graft block copolymerisation	Increased breaking strength; increase in elongation	[76]
Ditto	Polybutadiene + metals (Zn, Mg)	Extrusion; $T = 170$–210 °C	Graft block copolymerisation; structure formation	Increase in density; improvement of fluidity; improvement of resistance to thermo-oxidative influences	[77]
»	Butadiene-styrene copolymer	$F_M = 1.5 \times 10^9$ dyn cm^{-2}	Ditto	Increase in breaking strength	[78]
»	Isoprene-styrene copolymer	Ditto	»	Ditto	[78]
»	Epoxide oligomers	Rolling; $T = 130$–140 °C	Graft block copolymerisation; structure formation	Improvement in mechanical strength	[79]
Polypropylene	Poly(ε-caprolactam)	Extrusion; $T = 200$–210 °C	Ditto	—	[80]
Ditto	Methyl acrylate–sodium alkane-sulphonate copolymer	Extrusion; $F_{cut} = 1.5 \times 10^9$ dyn cm^{-3}	»	Improvement in susceptibility to dyeing	[82]
Polypropylene	Styrene-styrenesulphonamide copolymer	Ditto	»	Ditto	[82]
Poly(vinyl chloride)	Butadiene–acrylonitrile copolymer	Extrusion	Graft block copolymerisation	Improvement in impact strength	[88]
Ditto	Ditto	Rolling; $T = 150$–190 °C	Graft block copolymerisation; structure formation	Improvement in breaking and impact strength	[84–86]
»	Polyurethane elastomers	Ditto	Ditto	Ditto	[84–86]
Butadiene–styrene elastomers, butadiene–acrylonitrile copolymer	Thermoreactive resins of the resol type	Plasticisation of Brabender plastograph	»	»	[87]
Raw rubber or rubber soles (waste)	Phenol-formaldehyde resins	Rolling	Graft block copolymerisation	»	[88, 89]

Notation: F_M = mechanical force, F_{cut} = cutting force.

($T = 0$– -40 °C). The rigidity of the system, which is the main condition for treatment in accordance with this principle, was ensured by the presence of a polyamide component and also by the temperatures employed.[76]

In both cases the main result of the mechanosynthesis is that the polyolefin base becomes insoluble in specific solvents. In the pairs investigated, PE is the component responsible for structure formation, while grafting-block copolymerisation increases the mechanical strength and thermal stability.[78–80] The impact strength and resistance to rupture of poly(vinyl chloride) (PVC) improved appreciably on coextrusion of plasticisation of this polymer on rollers in the presence of elastomers[84–87] (Tables 5 and 6).

The intense influences to which the PVC–elastomer systems are subjected during treatment on rollers favour the occurrence of the grafting–block copolymerisation–structure formation reactions (Table 6). An increase in temperature promotes mainly the occurrence of the structure formation reaction, which ensures an increase in the resistance to rupture, whilst maintenance at low temperatures stimulates mechanochemical grafting–block copolymerisation, which is responsible for an appreciable growth of impact strength. In all the cases investigated, it was possible to establish a 100% increment in the resistance to rupture and impact strength, which is an outstanding result bearing in mind that in the most common cases the factors which improve one of these characteristics impair the other. The solution of equations expressing the dependence of the mechanochemical properties of the reaction products on the thermomechanical conditions made it possible to establish the optimum conditions for the treatment of a PVC–elastomer mixture on rollers.[85–87]

Mechanosynthesis in a polymer–polymer system (in the case of the system comprising waste from rubber articles and thermoreactive resins) leads to the formation of materials with improved physicomechanical properties.[87–89]

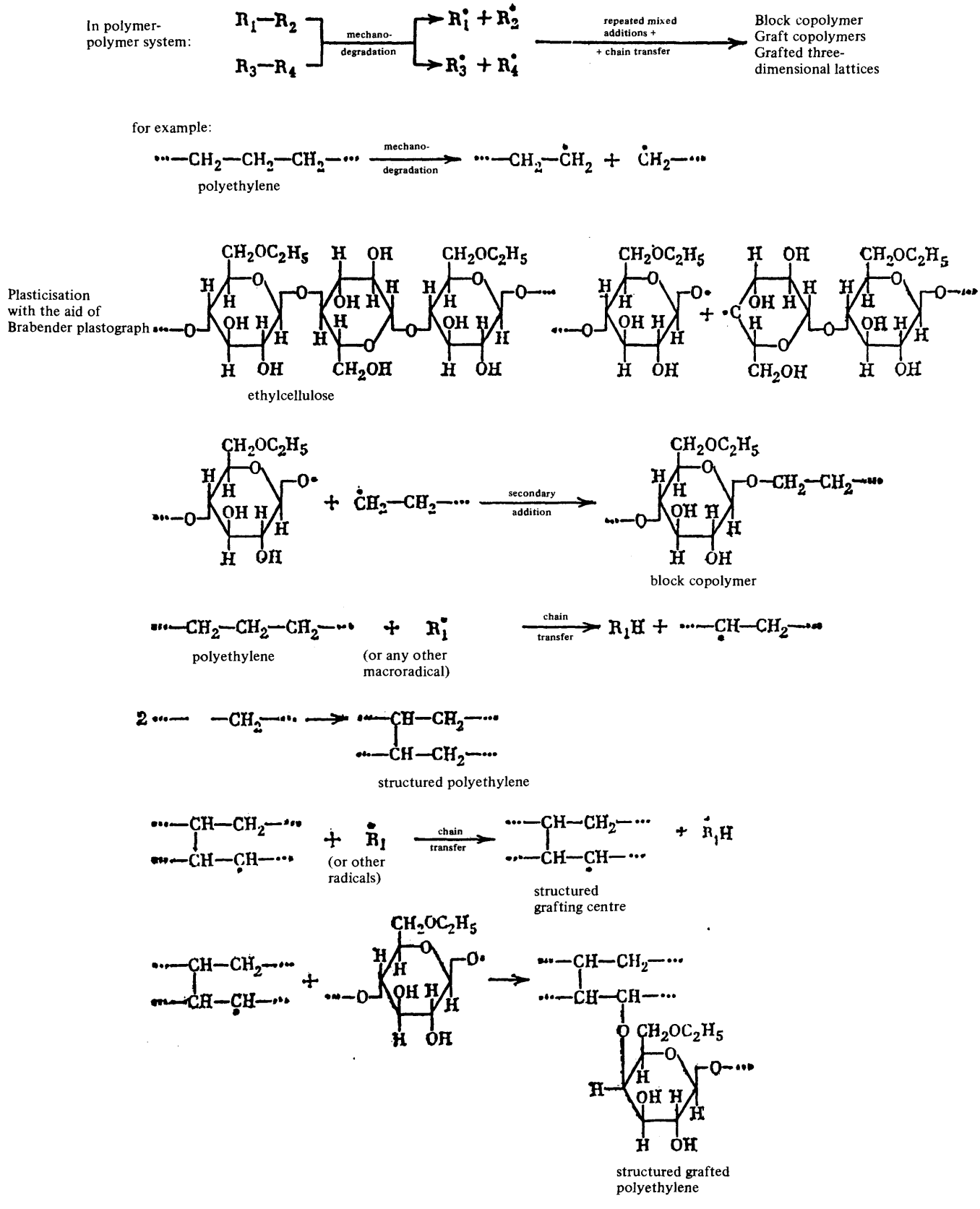


Figure 7. Mechanochemical reactions occurring in the mechanosynthesis in a polymer–polymer system.

III. REACTIONS INITIATED ON INORGANIC MECHANO-ACTIVATED SURFACES

1. Mechanochemical Grafting on Inorganic Surfaces

The mechanochemical activation of inorganic surfaces and the ability of such surfaces to activate chemical reactions have already long been known.[90-106] During the last decade, much attention has been devoted to the study of the mechanisms of these reactions and the elucidation of the nature of the centres inducing them.

Table 6. Variation of certain physicomechanical properties (%) of the PVC–elastomers systems as a function of the conditions of treatment*.[86-87]

Parameters of treatment on rollers*	Value of parameter	Nitrile rubber (SKN-18)		Polyurethane rubber	
		σ_p	a_k	σ_p	a_k
Duration of treatment, min (at $T = 170$ °C)	7	118	138	115	200
Ditto	14	117	258	115	136
"	21	116	233	115	156
Temperature of treatment, °C (for $\tau = 14$ min)	150	120	172	117	148
Ditto	170	117	258	115	136
"	190	115	90	119	216

Notation: σ_p is the resistance to breaking and σ_k the impact strength.
*For the system with 8% SKN and 2.5% PVC

The disintegration of ionic crystals such as those of $CaCO_3$, $BaSO_4$, rock salt, KCl, LiF, and CaF_2 leads to their activation, the degree of which has been estimated from their electron-donating capacity measured by EPR spectroscopy.[107] The surfaces obtained as a result of the grinding of the crystals are characterised by the emission of electrons and by the ability to initiate the grafting of certain vinyl monomers, especially styrene.[107-109]

The correlation between the change in the intensity of the electron emission during the mechanical breakdown *in vacuo* of ionic crystals (NaCl, LiF) and the degree of grafting of polystyrene to the newly formed surfaces indicates a shift in the development of these two effects, namely the grafting continues for a long time after the electron emission has ceased (Fig. 8). Consequently the initiation of the graft polymerisation is induced by the radicals generated on these surfaces by the electronic charges which persist for a long time after the rupture of the crystals.[107] Thus one may speak of an after-effect associated with the reactivity of the electrically charged active centres on the surfaces of the dispersed crystals.

In order to discover the nature of the active centres initiating polymerisation, a study was made of the influence of water vapour on the course of the grafting process. The moisture content of the crystal and the area of its contact surface with the monomer proved to be decisive factors for the process. For each type of crystal, there is a range of moisture contents within which the electrical potential and the degree of grafting reach a maximum. There exists therefore a selective catalytic influence exerted by the amount of water vapour which determines the reactivity of the inorganic surface newly formed as a result of the break up of the crystals.[110] On the other hand, the disintegration of such crystals *in vacuo* (10^{-6} mmHg) in the absence of moisture does not induce grafting. Consequently the adsorption of water vapour on electrical centres favour the formation of the polymerisation initiator. Under the influence of the static electricity on the mechanodispersed crystal surface, the water molecules dissociate and the resulting hydrogen ions ensure the cationic initiation of the polymerisation of styrene. The introduction of hydroquinone into the reaction medium does not disturb the grafting process, which is an additional argument in support of the cationic mechanism.

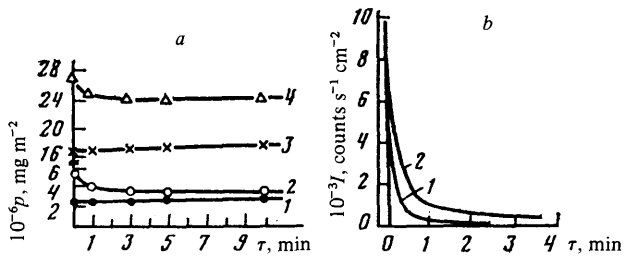


Figure 8. *a*) Dependence of the specific degree of grafting p of polystyrene on time τ after the breaking of the crystal in the liquid monomer and in argon with subsequent immersion in the monomer [1) and 2) NaCl; 3) and 4) LiF]; *b*) time decay of electron emission I from different crystals [1) NaCl; 2) LiF].[107]

Together with the grafting on the surface, homopolymerisation takes place on a limited scale; a radical mechanism has been attributed to such homopolymerisation on the basis of the observed consumption of hydroquinone. Presumably these two reactions—grafting and homopolymerisation—have a common initiation mechanism involving the active centres formed on the inorganic surface. In those cases where the degree of polymerisation of the grafted chains exceeds a certain specific value, the chains undergo homolytic rupture and the mechanoradicals formed combine with hydroquinone. Styrene, which is a nucleophilic monomer, should react with the positively charged centres formed as a result of the dissociation of water vapour. The polymer macromolecules should enter into a physical interaction with the negatively charged centres present on the surfaces formed.

This mechanism has been confirmed by the unipolar character of the charge arising on the surface produced by the breaking of the LiF crystals. When the crystals are broken into two parts, the corresponding rupture surfaces carry charges of opposite sign at the contact points, which results in the formation of a mosaic pattern in the charge distribution on the surface (Fig. 9).

The degree of grafting of styrene relative to the overall area of the negatively charged surface exceeds the degree of grafting relative to the area of the positively charged surface. Furthermore, fluorescence analysis of the products grafted on KCl powders established that the K and Cl contents in the grafted polystyrene are respectively 0.27 and 0.71%; this indicates the breakdown of the stoichiometric composition of the support, which can be explained by the irreversible

interaction of the polystyrene macromolecules with halide ions and the negatively charged centres on the newly formed surfaces of the crystal.

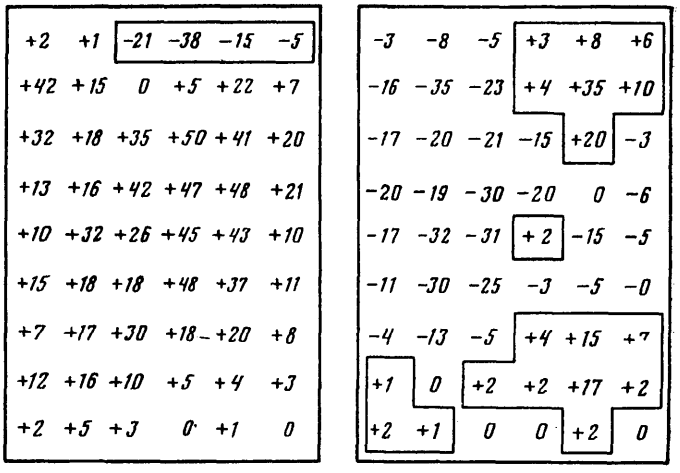


Figure 9. Topography of the distribution of electric charges on the surface of LiF crystals (5 × 10 mm² surface); the numerals indicate the charge intensity in 10^8 e cm^{-2}. [110]

The mechanochemistry of the quartz and sand surfaces is being vigorously investigated, but the existing contradictions have not yet been eliminated from this field. The main problem in the given instance is the elucidation of the nature of the active centres. It has been shown that, firstly, the mechanodispersion of quartz at a residual pressure of 10^{-3} to 500 mmHg in the presence of hydrogen at 80–400 K entails the dissociative chemisorption of hydrogen. [52–54] The active centres combining with hydrogen are formed both as a result of the mutual friction between these particles. The adsorbed hydrogen is firmly attached to the inorganic surface and its removal is possible only on raising the temperature to 600–700 K. On the basis of NMR and IR spectroscopic data, the reaction between quartz and hydrogen can be represented schematically as follows: [101]

$$\equiv Si-O-Si\equiv + H_2 \rightarrow \equiv SiH + SiOH \ .$$

The reaction is caused not only by radicals, which can be detected by EPR, but also by mechanoexcited $\equiv Si-O-$ bonds, since the total number of active centres on the surface is an order of magnitude higher than the surface concentration of free radicals (10^{13} cm^{-2} compared with 10^{12} cm^{-2}).

The primary act in the mechanochemical reaction between quartz and oxygen is the addition of O_2 to the radicals $\equiv \dot{S}i$ obtained on dissociation of the $\equiv Si-O-$ bond: [103]

$$\equiv Si-O-Si\equiv \xrightarrow[E_m]{} \equiv \dot{S}i + \dot{O}Si\equiv Si + O_2 \rightarrow SiOO^{\cdot} \ ,$$

$$\equiv SiOO^{\cdot} + {}^{\cdot}OSi \xrightarrow{\text{recombination}} \equiv SiOOOSi\equiv$$

peroxy-compound .

where E_m is the mechanical energy. The scheme presented above agrees with the consumption of oxygen and the concentration of paramagnetic centres. There is a possibility of the thermal decomposition of the final peroxy-compound:

$$\equiv SiOOOSi \xrightarrow{\Delta} \equiv SiOSi\equiv + O_2 \ .$$

This reaction explains the thermal desorption of oxygen at high temperatures.

Table 7. The adsorption characteristics of certain organic compounds in the vibromilling of sand.

Compound	s, Å²	$10^{-18}N_1$, molecules g^{-1}	$10^{-18}N_{50}$, molecules g^{-1}	N_1+N_{50}, m² g^{-1}
$CH_2=C(CH_3)COOCH_3$	34.3	3.0	4.9	2.7
$(CH_3)_2CHCOOCH_3$	36.1	2.1	1.3	1.2
$CH_2=CHCOOCH_3$	30.8	3.1	4.6	2.4
$C_6H_5COOCH_3$	32.1	2.7	1.2	1.2
$CH_3COOCH=CH_2$	31.2	2.7	1.0	1.2
$CH_3COOC_2H_5$	32.5	2.7	1.0	1.2
$CH_2=CH(CH_2)_4CH_3$	41.4	1.6	0.57	0.91
p-C_7H_{16}	42.5	1.3	0.57	0.80
$(CH_3)_2CO$	28.9	3.3	1.2	1.2
p-$C_2H_5NH_2$	29.0	4.1	2.5	1.9
$(p$-$C_3H_7)_2NH$	40.7	2.8	1.6	1.8

Notation: s is the area of the molecules, N_1 the number of molecules adsorbed per mole of SiO_2, and N_{50} the same number after milling for 50 min.

The mechanical activation of the SiO_2 surfaces can also be accounted for by the grafting of certain vinyl and acrylic monomers in the vapour state (Table 7). [111] Under milling conditions, the monomers gradually polymerise on the solid surface. Oxygen exerts an inhibiting effect on this reaction, while the adsorption of the vapours of organic compounds has no influence on it whatsoever, which indicates a radical character of the process. Although free radicals were not detected under the experimental conditions (by EPR), milled sand contains numerous electrons in the surface traps while the adsorption of organic vapours induces exo-electron emission. [112] Homose et al. [111] therefore proposed a mechanism for the process which begins with electron transfer to the adsorbed monomer, attached to the surface by hydrogen bonds, with the subsequent formation of a radical-ion, which induces in its turn a reaction involving radicals.

2. Mechanochemical Homopolymerisation and Copolymerisation

Evidence confirming the idea that mechanical energy can induce the polymerisation reaction was obtained as a result of studies on polymers in the solid phase. Adler et al. [112] concluded that the elimination of rigorous order from the structure of the crystal lattice influences significantly the the rate of propagation of this type of polymerisation. With the aid of microscopy in polarised light, they demonstrated that polymerisation takes place precisely at the edges of the crystal irregularities. As the polymer is formed, the volume of the lattice diminishes and mechanical stresses appear in it favouring the dissociation of chemical bonds. Under these conditions, new active centres arise in the reaction medium and accelerates the polymerisation, which is initiated in most cases by radiation. Hence it follows that the mechanochemical act plays a significant role in the successful carrying out of the polymerisation process in the solid phase.

Another argument in support of the mechanochemical hypothesis concerning the solid-phase polymerisation is provided by experiment of Bamford et al. [113] involving the

grinding of acrylic and methacrylic acid crystals.[113] These crystals are subjected to a pressure of 1–5 atm directed at right angles to the axis of the crystal lattice. After irradiation with UV light, it was established that the polymerisation takes place without initiators precisely in the regions where the crystals were ground. Thus the idea was put forward that for this type of polymerisation the role of the mechanochemical act is not confined to that of an accelerating factor, because it can also induce initiation. Subsequently, using the energy of a high-intensity shockwave,[114,115] the ability of mechanical energy to induce true polymerisation involving all the stages of the chain mechanism was demonstrated.

Kargin and co-workers[116] used vibration dispersion for the polymerisation of a solid monomer—sodium acrylate. The authors assumed that the process was initiated by the concentration of mechanical energy on structural defects. The energy-induced transition of an electron located in the immediate vicinity of the COO^- group, involving an electron vacancy in one of the lattice sites, leads to the formation of a radical.

Under the experimental conditions used in the above study,[116] acrylamide did not polymerise, so the authors concluded that the ionic nature of the crystal lattice of the monomers plays a significant role.

A number of investigators[117–122] developed a polymerisation method which is activated by "mechanoinitiators"—inorganic crystalline salts with uncompensated electrons, the so-called "electron traps". Under the conditions of vibration dispersion, these electrons migrate to the newly formed surfaces and initiate polymerisation.

Subsequently it was possible to carry out the polymerisation and copolymerisation of a large number of a wide variety of monomers under the conditions of vibromilling without initiating additives. The starting materials (vinyl, acrylic, diene, and cyclic monomers or monomers which cannot be polymerised by the usual methods), were used in the solid (acrylamide, ε-caprolactam, etc.) or liquid state.[123–129]

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Substitutional Carbonylation of Organic Compounds Catalysed by Palladium Complexes

Yu.V.Gulevich, N.A.Bumagin, and I.P.Beletskaya

The results of studies on the catalytic carbonylation of organoelemental compounds, organic halides, and other substrates of the type RX, in which X is substituted by CO during the reaction, are analysed. The mechanism of the action of palladium carbonylation catalysts is examined and the principal applications of the substitutional carbonylation reactions in organic synthesis are indicated.
The bibliography includes 141 references.

CONTENTS

I. Introduction 299
II. Carbonylation of organoelemental compounds 300
III. Carbonylation of organic halides 303
IV. Carbonylation of other organic substrates 311

I. INTRODUCTION

Among the selective methods for the preparation of oxygen-containing organic compounds, catalytic methods involving carbon monoxide play a special role. This industrially important field of homogeneous catalysis was founded as a result of the studies by Roelen[1] and Reppe[2] at the end of the 1930's and the beginning of the 1940's. Roelen showed that, in the presence of cobalt-containing catalyst, alkenes interact with CO and H_2 to form aldehydes with linear and branched structures containing one carbon atom more than the initial alkene:

$$RCH=CH_2+CO+H_2 \rightarrow RCH_2CH_2CHO+RCHMeCHO\,.$$

Reppe discovered a series of related reactions involving the carbonylation of alkenes, alkynes, and alcohols catalysed by carbonyl compounds of Group VIII metals. The products of these reactions are carboxylic acids, their derivatives, or alcohols, for example:

$$CH_2=CH_2+CO+H_2O \rightarrow EtCO_2H\,,$$
$$CH\equiv CH+CO+ROH \rightarrow CH_2=CHCO_2R\,,$$
$$MeCH=CH_2+CO+H_2O \rightarrow BuOH+CO_2\,.$$

After the publication of the above studies,[1,2] vigorous investigation of the reactions of organic compounds with carbon monoxide in the presence of transition metal complexes began. As a result, procedures such as the carbonylation of olefins, acetylenes, polyunsaturated compounds, alcohols, and nitrogen-containing compounds have been converted into large and independent branches of the catalytic chemistry of CO. The experimental data accumulated in this field as well as examples of the industrial use of the above reactions have been reflected in numerous monographs and reviews (see, for example, Refs.3–9).

The present review deals with the development of a comparatively new aspect of the chemistry of CO, which is of interest mainly for fine organic synthesis – the catalytic carbonylation of organoelemental compounds, organic halides, diazonium salts, arenes, and other substrates of the type RX (X = M, Hal, N_2BF_4, H, etc.). We have designated these reactions by the term "substitutional carbonylation", because the interaction of carbon monoxide with the substrates RX results in the substitution of the group X by the fragment CONu. Depending on the nucleophilic coreactant (Nu^-)

used, various carbonyl-containing products RCONu are formed—carboxylic acids and their derivatives, aldehydes, and ketones. Typical examples of such reactions are presented below:

$$RHal+CO+R_2'NH\rightarrow RCONR_2'+HHal,$$
$$RHgOAc+CO+R'OH\rightarrow RCO_2R'+HOAc+Hg,$$
$$RN_2BF_4+CO+R_4'Sn\rightarrow RCOR'+R_3'SnBF_4+N_2.$$

The complexes of a number of transition metals, namely palladium, nickel, cobalt, and rhodium, have been used as catalysts of the substitutional carbonylation of organic compounds. The substitutional carbonylation reactions have been studied most widely and in greatest detail under the conditions of homogeneous catalysis by palladium compounds. We have confined ourselves in the present review to other catalytic systems only when their application provides definite advantages compared with palladium complexes.

II. CARBONYLATION OF ORGANOELEMENTAL COMPOUNDS

Organic derivatives of many non-transition elements are known[3] to react with CO, forming a wide variety of oxygen-containing compounds. Unfortunately, such reactions can usually be achieved only under severe conditions (high CO pressure and temperature) and frequently proceed with a low selectivity. In many instances it is possible to overcome these difficulties by using palladium complexes as carbonylation catalysts. Catalytic carbonylation was first achieved for organic derivatives of mercury,[10] whose reactions with CO have now been most thoroughly investigated and have found applications in organic synthesis.

1. Reactions of Organomercury Compounds

It was noted in 1968[10] that, in the presence of stoichiometric amounts of $PdCl_2$, the aryl derivatives of mercury Ar_2Hg and ArHgCl interact with CO under very mild conditions: 1 atm and 20 °C. The reaction products are the acid chlorides ArCOCl when the carbonylation is carried out in an inert solvent or the esters $ArCO_2R$ when an alcohol is used as the coreactant:

$$Ph_2Hg+PdCl_2 \xrightarrow[MeCN]{CO} \underset{21\%}{PhCOCl}+HgCl_2+Pd,$$
$$4\text{-}MeC_6H_4HgCl+PdCl_2 \xrightarrow[MeOH]{CO} \underset{27\%}{4\text{-}MeC_6H_4CO_2Me}+HgCl_2+Pd.$$

As a result of the reaction, palladium(II) passes to the zero oxidation state. The application of a suitable oxidant, for example, $CuCl_2$, makes it possible to regenerate palladium(II) ($Pd + CuCl_2 \rightarrow PdCl_2 + Cu_2Cl_2$) and make the carbonylation catalytic:

$$ArHgCl \xrightarrow[CuCl_2,\ HOAc]{10\%\ PdCl_2,\ 1\ atm\ CO} ArCO_2H,$$

Ar = 4-MeC_6H_4 (31%), 4-$HO_2CC_6H_4$ (56%),

In some cases, symmetrical diaryl ketones are formed in considerable amounts together with carboxylic acid derivatives (1—4 atm CO, 20 °C):[11]

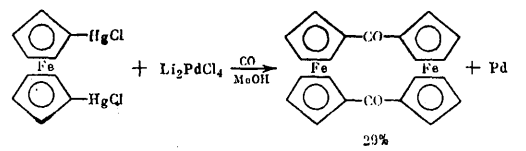
$$PhHgCl \xrightarrow[CuCl_2,\ MeCN]{10\%\ LiPdCl_4,\ CO} \underset{22-40\%}{PhCOCl}+\underset{11-29\%}{Ph_2CO}.$$

Kasahara and co-workers[12,13] achieved for the first time the carbonylation of organomercury derivatives of non-benzenoid aromatic systems—ferrocene, furan, and thiophen (50 atm CO, 70—100 °C):

$$ArHgCl+Li_2PdCl_4 \xrightarrow[MeOH]{CO} \underset{30-35\%}{ArCO_2Me}+\underset{32-40\%}{Ar_2CO}+Pd,$$

where Ar = ferrocenyl, 2-furyl, 2-(5-methoxycarbonylfuryl), and 2-thienyl.

They used the method developed for the single-stage synthesis of [1.1]ferrocenophane-1,12-dione from readily available 1,1'-di(chloromercuri)ferrocene:[12]



29%

The reaction of arylmercury acetates with CO in the presence of $Pd(OAc)_2$ (one equivalent) and added sodium acetate (two equivalents) takes place selectively at 1 atm in methanol or trifluoroacetic acid and leads to the formation of the methyl esters or anhydrides of arenecarboxylic acids respectively in high yields,[14] for example:

$$PhHgOAc+Pd(OAc)_2 \xrightarrow[NaOAc,\ MeOH]{CO} \underset{88\%}{PhCO_2Me}+Hg(OAc)_2+Pd,$$
$$PhHgOAc+Pd(OAc)_2 \xrightarrow[NaOAc,\ CF_3CO_2H]{CO} PhCO_2Ac \xrightarrow[2)\ CH_2N_2]{1)\ H^+/H_2O} \underset{86\%}{PhCO_2Me}.$$

We may note that the initial organomercury compounds can be synthesised by mercurating the corresponding arenes with mercury(II) acetate and can be used in the subsequent carbonylation without isolating them from the reaction mixture.

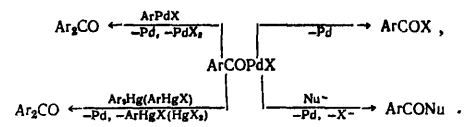
The active intermediates in the reactions of arylmercury(II) compounds in the reactions with CO described above are undoubtedly organic palladium σ-complexes, formed in the first stages of the process:[15]

$$Ar_2Hg+PdX_2\rightarrow ArPdX+ArHgX,$$
$$ArHgX+PdX_2\rightarrow ArPdX+HgX_2,$$
$$X=Hal,\ OAc.$$

In a CO atmosphere, the arylpalladium complex is readily carbonylated, affording acyl derivatives:[16,17]

$$ArPdX+CO\rightarrow ArCOPdX.$$

The possible pathways in the subsequent conversion of ArCOPdX into the final carbonyl-containing organic products are presented in the scheme below:[10,11,18]



The reductive elimination of ArCOPdX leads to ArCOX. In the presence of a nucleophilic coreactant (Nu^-) in the reaction mixture, its interaction with ArCOX or with ArCOPdX produces the carboxylic acid derivatives ArCONu. Symmetrical diaryl ketones are formed in the reaction of the acyl complex with the initial organomercury compounds or with the σ-aryl derivative of palladium. Carbonylation of organomercury compounds is frequently complicated by oxidation processes, which lead to the side products Ar_2, ArCl, etc.

The reactions of aryl derivatives of mercury with CO, catalysed by phosphine complexes of palladium, are of great interest from the synthetic point of view. These reactions are fairly selective, and, in contrast to those examined previously, are catalytic in relation to the palladium complex in the absence of specially added oxidants. Thus, on catalysis with 0.5—2 mole% $PdCl_2(PR'_3)_2$ (R' = Ph or Bu), organomercury salts of the benzene and naphthalene series

interact with CO and alcohols to form esters of arenecarboxylic acids:[19,20]

$$ArHgX \xrightarrow[70-110^\circ C,\ ROH]{\text{"Pd", 4-10 atm CO}} ArCO_2R + Hg, \quad 30-99\%$$

X=OAc, O_2CCF_3

R=Me, Et, n-C_8H_{17}, iso-Bu, CH_2=$CHCH_2$, Ph

ArHgX containing chlorine, methoxy-, methoxycarbonyl, dimethylamino-, and acetamido-groups in the aromatic ring readily enter into the reaction. Primary unsaturated alcohols, allyl alcohol, and phenol can be used as the nucleophilic coreactants. We may note that the reaction is sensitive to steric hindrance: the use of sterically hindered organomercury compounds or secondary or tertiary alcohols reduces appreciably the yield of the ester and leads to the preferential formation of ArH and $ArCO_2H$.

The conversion of the organomercury compounds ArHgX and Ar_2Hg into symmetrical diaryl ketones has been achieved under very mild conditions (1 atm CO, 20 °C) by using a system comprising metal complex and nucleophilic (I^- ion) catalysts and by carrying out the carbonylation in inert solvents [hexamethylphosphoramide (HMP), tetrahydrofuran (THF), and acetone]:[21,22]

$$ArHgX \xrightarrow[Bu_4NI]{1\%\ PhPd(PPh_3)_2I,\ CO} Ar_2CO + HgX_2 + Hg, \quad 78-99\%$$

X=Cl, Br, OAc

$$Ar_2Hg \xrightarrow[Bu_4NI \text{ or } NaI]{0.5\%\ [Rh(CO)_2Cl]_2,\ CO} Ar_2CO + Hg, \quad 77-90\%$$

These reactions can serve as convenient methods of synthesis of substituted benzophenones $(YC_6H_4)_2CO$ (Y = H, 4-Me_2N, 4-H_2N, 4-MeO, 4-Me, 4-Cl, or 2-HO). The method is also applicable to the synthesis of heterocyclic ketones, which has been demonstrated for the conversion of 2-thienylmercury bromide into $(2\text{-}C_4H_3S)_2CO$.

The mechanism of the carbonylation of aryl derivatives of mercury in the presence of phosphine complexes of palladium differs from that presented above. The catalytically active species in the given case is the zerovalent palladium derivative PdL_2 (L = phosphine ligand) obtained by the reduction of the initial palladium complexes by organomercury compounds. As an example, the scheme for the catalytic cycle involving the formation of diaryl ketones by the carbonylation of organomercury compounds in the presence of $PhPd(PPh_3)_2X$ is presented below:[22]

$$PhPdL_2X + RHgX \rightarrow PhR + HgX_2 + PdL_2,$$

$$RHgX + PdL_2 \rightarrow RPd(HgX)L_2 \rightarrow RPdL_2X + Hg;$$

or

$$RHgPdL_2X$$

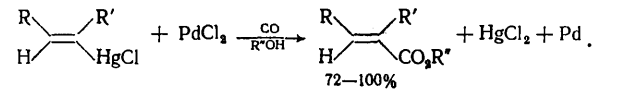
$$RPdL_2X + CO \rightarrow RCOPdL_2X$$

$$RCOPdL_2X + RHgX \rightarrow RCOPdRL_2 + HgX_2,$$

$$RCOPdRL_2 \rightarrow RCOR + PdL_2.$$

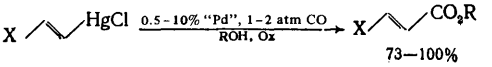
As a result of the oxidative addition of the organomercury salt to PdL_2 (the insertion of the zerovalent palladium complex in the Hg–C or Hg–X bond[23]) and the elimination of metallic mercury, the aryl derivative of palladium $RPdL_2X$ is obtained. The carbonylation of $RPdL_2X$ and the subsequent transmetallation reaction give rise to the diorganic complex $RCOPdRL_2$. The reductive elimination reaction of the latter leads to a ketone and the initial catalytically active PdL_2 species. We may note that the above scheme shows only one of the possible pathways leading to the formation of ketones in the carbonylation of organomercury salts. Clearly, the reaction involving the exchange between RHgX and $RPdL_2X$ can precede the insertion of CO in the C–Pd bond and metallic mercury may be eliminated in the last stages of the process. The addition of the iodide ion plays an important role. The I^- ion apparently accelerates[22] the exchange reaction of $RCOPdL_2X$ with RHgX (nucleophilic catalysis[24]) and facilitates the insertion of the zerovalent palladium complex in the Hg–C or Hg–X bond.

The use of vinyl derivatives of mercury as the initial substrates in the carbonylation reactions opens up pathways to the synthesis of αβ-unsaturated carbonyl compounds. Thus vinylmercury chlorides react with CO and $PdCl_2$ (one equivalent) in the presence of water or alcohols, forming αβ-unsaturated carboxylic acids or their esters in high yields (1 atm CO, -78–20 °C):[18]



R, R′=Alk, Ar, vinyl; R″=H, Me, Et

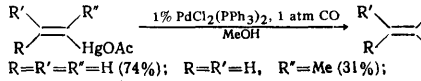
The carbonylation takes place with complete retention of the configuration of the vinyl fragment. By adding oxidants for zerovalent palladium [copper dichloride[18] or iron(III) chloride[25]], it was possible to make the reaction catalytic:



«Pd»=$PdCl_2$, Pd/C; Ox=$CuCl_2$, $FeCl_3$

X=Cl, Ph, Bu; R=H, Me, Et, Pr

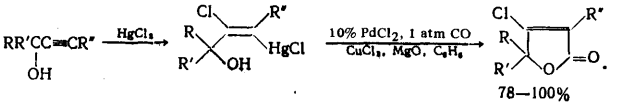
The need to add oxidants disappears when the process catalysts are phosphinepalladium complexes:[19,20]



R=R′=R″=H (74%); R=R′=H, R″=Me (31%); R=R′=Ph, R″=H (36%)

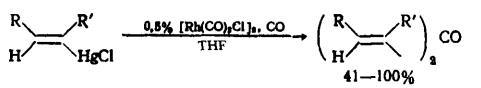
The cause of this phenomenon, which arises from the reaction mechanism, were considered in our previous communication in relation to the carbonylation of aryl derivatives of mercury.

If the organomercury compound contains the hydroxy-group, then under certain steric conditions the latter can behave as the nucleophile in the carbonylation process. Such a reaction results in intramolecular cyclisation, which leads to the formation of a lactone. This precise idea has in fact been the basis of an elegant method of synthesis of β-chloro-$\Delta^{\alpha\beta}$-butenolides, which involves two stages: the mercuration of propargyl alcohols and the subsequent carbonylation of the resulting organomercury derivatives:[26,27]



The yield of the lactone increases when the reaction with CO is carried out in the presence of magnesium, which binds the HCl evolved.

Symmetrical divinyl ketones have been synthesised by carbonylating vinylmercury chlorides at 1 atm at 25 °C in THF in the presence of a rhodium catalyst:[28]

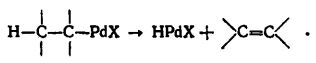


R=H, Ar, Alk; R′=H, Alk

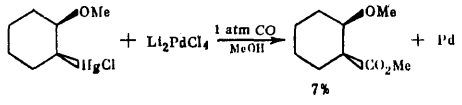
The possibility of using palladium complexes as catalysts in this reaction has not been investigated.

The interaction of alkylmercury compounds with CO has been studied comparatively little. The difficulty of carrying out the reaction is associated with the instability of the intermediate alkyl

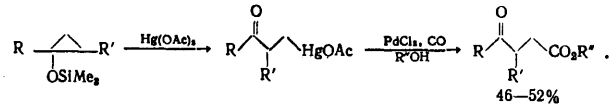
complexes of palladium and other transition metals, which tend to undergo a rapid β-elimination reaction:



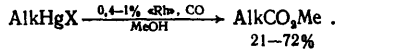
As a result of this side process, the yield of the carbonylation products is usually low:[29]



The undesirable elimination reaction can be avoided by using initial substrates containing an electron-accepting substituent in the β-position relative to the mercury atom. Thus β-acetoxymercuriketones interact with $PdCl_2$ (one equivalent) and alcohols in a CO atmosphere, forming γ-ketoacid esters in satisfactory yields:[30]



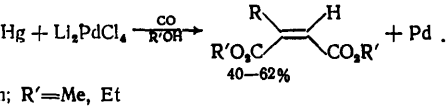
The carbonylation of alkylmercury(II) derivatives in methanol at an elevated CO pressure (2–63 atm), catalysed by $(Ph_3P)_3RhCl$, leads to methyl esters of alkanecarboxylic acids, the yield of the latter reaching 72%:[19,20]



X = OAc, Br
Alk = Et, n-C_6H_{13}, n-$C_{12}H_{25}$, $MeCO_2(CH_2)_2$, $BuCH(OMe)CH_2$, 2-methoxycyclohexyl

The examples presented make it necessary to revise the initial sceptical attitude towards the synthetic possibilities of the reactions of alkyl derivatives of mercury with CO and show that it is essential to investigate them more widely. The synthetic use of the stereoselectivity of this reaction, which proceeds with the preferential retention of the configuration at the carbon atom linked to the metal, is promising.[29]

Dialkynylmercurys interacts with CO in an alcoholic medium at 20 atm and 25 °C with formation of a substituted maleate as the main product:[31]



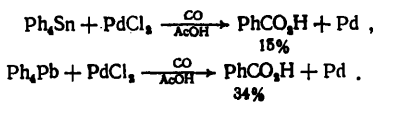
R=Et, Ph; R'=Me, Et

The authors believe that $RC{\equiv}CCO_2R'$ is formed in the first stage of the process and subsequently undergoes hydroalkoxycarbonylation.

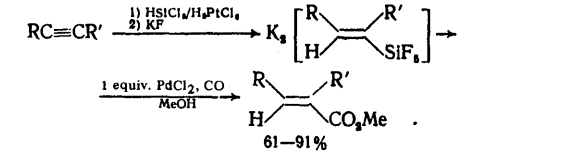
2. The Reactions of Other Organoelemental Compounds

The carbonylation of other organoelemental compounds has been studied to a much lesser extent.

Tetraphenyl-tin and tetraphenyl-lead react with CO and palladium chloride at 1 atm and 20 °C in acetic acid with formation of benzoic acid, but the yields are low in both reactions:

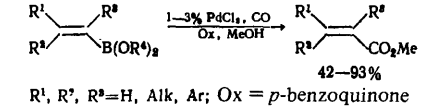


The carbonylation of the readily available vinyl derivatives of silicon–(*E*)-alkenylpentafluorosilicates– was achieved.[32] The reaction takes place stereospecifically and leads to high yields of the esters of (*E*)-αβ-unsaturated carboxylic acids (1 atm CO, 25 °C):



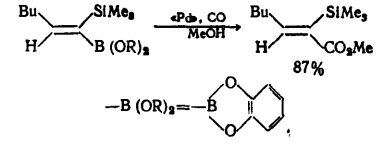
It is noteworthy that, in contrast to alkenylpentafluorosilicates, the corresponding alkenyltrialkylsilanes are relatively unreactive: they are carbonylated at a low rate. Phenyl- and benzylpentafluorosilicates do not interact with CO under the conditions investigated.

A convenient method of stereocontrolled synthesis of αβ-unsaturated acid esters, based on the reaction of alkenylboronates with CO and methanol in the presence of palladium chloride (1 atm, 0 to 50 °C), has been proposed.[33] The use of *p*-benzoquinone as the oxidant for zerovalent palladium makes this reaction catalytic:

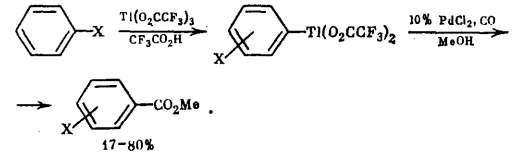


R¹, R², R³=H, Alk, Ar; Ox = *p*-benzoquinone

It is of interest that, when the initial substrate contains a silicon–carbon bond together with the boron–carbon bond, the former is not involved in the reaction:

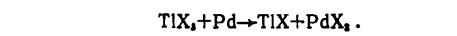


The carbonylation of the monoaryl compounds of thallium $ArTl(O_2CCF_3)_2$ in methanol leads to the methyl esters of arenecarboxylic acid (1 atm CO, 20 °C):[34,35]



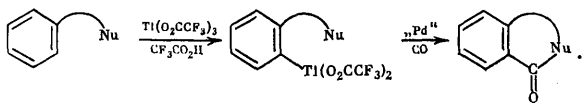
X = t-Bu, H, MeO, F, AcNH, H_2NCONH, PhCO

The reaction is catalytic with respect to palladium in the absence of specially added oxidants, because the thallium(III) salt, formed in the exchange interaction of organothallium derivatives with $PdCl_2$, regenerates the catalyst:

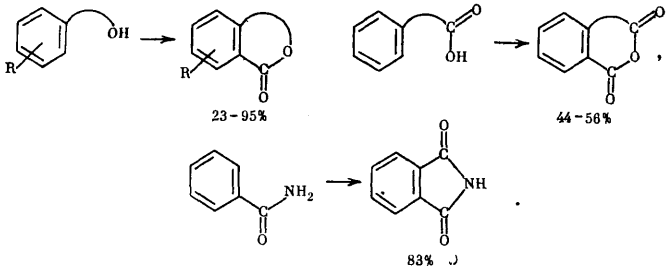


The initial arylthallium compounds can be obtained by the direct electrophilic substitution of thallium in arenes. This reaction is distinguished by high regioselectivity. Thus the fluorine atom and the t-Bu groups in methanol direct the attack by the thallium-substituting reagent almost exclusively to the *para*-position, while AcNH, PhCO, and other groups which are coordinated to the thallium(III) salt direct the attack to the *ortho*-position in the benzene ring. Among *ortho*-directing substituents, those which are capable of acting as nucleophiles in the carbonylation stage, for example CH_2OH, $(CH_2)_2OH$, CO_2H, $CONH_2$, etc. occupy a special

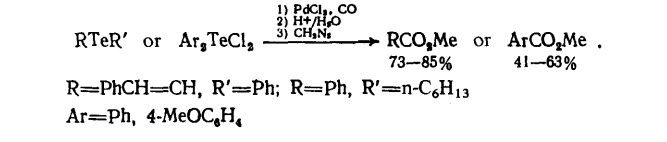
place. In this case the thallium substitution process and subsequent carbonylation result in intramolecular cyclisation:



The method has been used to synthesise a series of cyclic products—substituted γ- and δ-lactones, phthalic and homophthalic anhydrides, and phthalimide:[34,35]



The reaction of alkylbenzenes with CO (4—7 atm) in the presence of thallium trifluoroacetate and catalytic amounts of a palladium(II) salt leads to alkylbenzoic acids.[36] For example, a mixture of isomeric methylbenzoic acids has been obtained from toluene (*para*:*meta*:*ortho* = 91:5:4) in 81% yield relative to $Tl(O_2CCF_3)_3$ [Tl(III):Pd(II) ≃ 73:1]. The monoaryl derivatives of thallium(III), formed *in situ*, are in all probability intermediates in these reactions. The carbonylation of organic compounds of tellurium(II) and tellurium(IV) in the presence of stoichiometric amounts of $PdCl_2$ (1—20 atm CO, 20—30 °C) has been achieved in a recently published study:[37]



R=PhCH=CH, R′=Ph; R=Ph, R′=n-C_6H_{13}

Ar=Ph, 4-$MeOC_6H_4$

The reaction of the asymmetric telluride PhCH = CHTePh with CO leads mainly to an αβ-unsaturated acid ester, i.e. PhCH = $CHCO_2Me$. In the case of n-$C_6H_{13}TePh$, a benzoic acid derivative is formed, namely $PhCO_2Me$.

Thus the carbonylation of organoelemental compounds in the presence of palladium complexes makes it possible to obtain a wide variety of carbonyl-containing products. In many instances, these are chemoselective and stereoselective processes in which catalytic amounts of palladium compounds are used.

III. CARBONYLATION OF ORGANIC HALIDES

Not only organoelemental compounds but purely organic reagents can serve as sources of organic groups in substitutional carbonylation reactions catalysed by palladium complexes. Among such compounds, organic halides have found the widest application. The possibility of achieving reactions of this kind is based on the formation of σ-organopalladium compounds $RPdL_2X$ (L = ligand) as a result of the oxidative addition of the halide RX to a zerovalent palladium complex:[38—40]

$$PdL_n + RX \rightarrow trans\text{-}RPdL_2X + (n-2)L .$$

In view of the importance of the oxidative addition reaction for the understanding of the data described in this Section, we shall deal briefly with its main features.[40] Firstly, aryl and vinyl halides as well as benzyl, allyl, and certain other halides can be used in the reaction (in the case of alkyl halides containing a β-hydrogen atom, the organopalladium compounds formed are unstable and tend to undergo rapid β-elimination of palladium hydride). Secondly, the reactivity of the organic halides towards zerovalent palladium usually falls in the sequence RI > RBr > RCl. Thirdly, in the case of aryl halides, the rate of oxidative addition diminishes on passing from substrates containing electron-accepting groups to halogeno-derivatives containing electron-donating substituents. Fourthly, the reaction with vinyl halides proceeds with complete retention of the configuration of the vinyl group. Benzyl and allyl halides interact with zerovalent palladium complexes with the preferential inversion of the configuration of the carbon atom linked to the halogen. Finally, zerovalent palladium is used in the atomic state in the oxidative addition reactions. This can be achieved most simply by using zerovalent palladium complexes. As a result of oxidative addition, the coordination number of palladium increases by 2. Hence it follows that the initial zerovalent palladium complexes must be coordination-unsaturated or can readily dissociate under the reaction conditions.

The first communications concerning the carbonylation of organic halides under the conditions of catalysis by palladium compounds appeared in 1963—1964.[41—43] However, up to the middle 1970's, the number of studies were small and the initial substrates used were mainly allyl halides. The carbonylation occurred under severe conditions at high CO pressures and temperatures. Only after the discovery of the reaction involving the oxidative addition of organohalides to zerovalent palladium complexes[38] and the elucidation of the role which phosphine and certain other electron-donating ligands play in the stabilisation of intermediate organopalladium compounds, was it possible to reduce significantly the temperature and pressure at which carbonylation takes place and to extend the reaction to a wide range of organic halides.[44—48] Since then systematic research into the catalytic carbonylation of organic compounds began and this led to the development of new convenient methods of synthesis of a wide variety of carbonyl-containing products.

1. The Synthesis of Carboxylic Acids and Their Derivatives

The reaction of organic halides RX with CO catalysed by palladium complexes has found the widest application in the synthesis of carboxylic acids and their derivatives—esters and amides:

$$RX + HNu + CO \xrightarrow{«Pd»} RCONu + HX .$$

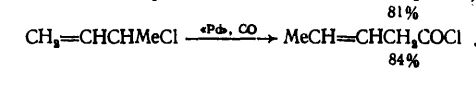
Nu=OH, OR′, NR'_2

Carbonylation without the addition of a nucleophilic coreactant has been least investigated and takes place under much more severe conditions with formation of carboxylic acid halide:

$$RX + CO \xrightarrow{«Pd»} RCOX .$$

For example, allyl chlorides and bromides interact with CO in the presence of a palladium catalyst at a pressure of 77—500 atm and a temperature of 80—150 °C in benzene or in the absence of a salt, forming the halides of αβ-unsaturated carboxylic acids.[42,43,49—51] The yield of the target product is fairly high under certain conditions and can become quantitative.[43] The palladium catalyst is usually added to the reaction mixture in the form of a π-allyl complex[43,50,51] or a palladium(II) salt.[42,49] The use of palladium black leads to the formation of a less active catalytic system.[43]

Despite the fact that the carbonylation can be accompanied by the allylic rearrangement, it is regioselective: only one product is obtained, in which the carbonyl group is linked to the least substituted carbon atom of the allyl fragment:[43,50]



In both reactions described above, the oxidative addition of the initial substrate to zerovalent palladium results in the formation of the same intermediate – bis(1-methyl-π-allylpalladium chloride).

In certain cases the carbonylation is complicated by the migration of the double bond in the acid halide from the βγ-position to the conjugated αβ-position:[49]

$$CH_2{=}CHCH_2Cl \xrightarrow{«Pd», CO} CH_2{=}CHCH_2COCl + MeCH{=}CHCOCl\ .$$

Allyl chlorides are less active than the corresponding bromides. Thus the rates of carbonylation of $CH_2=CHCH_2Cl$ and $CH_2=CHCH_2Br$ are in the ratio $1:\sim 0.08$ under identical conditions.[50] The structure of the allyl group also influences the reactivity of the halogeno-derivatives. The relative rates of the reaction increase in the sequence[50]

$$CH_2{=}CHCH_2Cl > MeCH{=}CHCH_2Cl \cong CH_2{=}CHCHMeCl > > \text{3-chlorocyclo-octene} \cong CH_2{=}CMeCH_2Cl > CH_2{=} {=}CHCHCl_2 \cong ClCH_2CH{=}CHCH_2Cl,$$

in the ratios 1:0.5: 0.04: 0.01.

The carbonylation of a mixture of allyl chloride and a conjugated diene leads to the formation of a derivative of the dienecarboxylic acid together with the chloride of a βγ-unsaturated acid,[50] for example:

$$CH_2{=}CHCH_2Cl + CH_2{=}CHCH{=}CH_2 \xrightarrow{«Pd», CO} \rightarrow \underset{36\%}{CH_2{=}CHCH_2COCl} + \underset{28\%}{CH_2{=}CH(CH_2)_2CH{=}CHCH_2COCl}.$$

Aryl, vinyl, benzyl, and alkyl chlorides, which are less reactive in the oxidative addition reaction, do not interact with CO under the conditions which are usually employed in the reactions of allyl chlorides.[43] The conversion of halogenoarenes into aroyl halides in the presence of palladium catalysts can be achieved at high temperature and CO pressures.[52,53] Thus arenecarboxylic acid fluorides have been obtained by carbonylating halogenoarenes at 300 – 350 °C and 600 – 900 atm in the presence of alkali metal fluorides:[53]

$$ArX + MF \xrightarrow[0.5-78\%]{«Pd», CO} ArCOF + MX,$$

"Pd" = $PdCl_2$ or Pd/C; M = alkali metals; X = F, Cl, Br, I

Summarising, one may say that the synthesis of the acid halides RCOX by the reaction of RX with CO is of limited importance and is applicable mainly to the synthesis of the halides of βγ-unsaturated acids from allyl halides. The catalytic cycle in the formation of RCOX apparently includes stages involving the oxidative addition of RX to zerovalent palladium, the insertion of CO in the C – Pd bond in the complex RPdX, and the reductive elimination of RCOPdX (we considered previously all the reactions of the palladium complexes incorporated in the cycle described). Under the conditions used in the synthesis of acid halides, palladium-containing intermediates readily decompose with the liberation of the relatively inactive palladium black. The reason for their instability is the absence from the reaction mixture of ligands capable of stabilising these palladium compounds. The deactivation of the homogeneous palladium catalyst necessitates the carrying out of the carbonylation of organic halides under very severe conditions. The carbonylation of allyl substrates is an exception, probably because of the high reactivity of allyl halides in the oxidative addition to zerovalent palladium and the stability of the π-allyl complexes of palladium obtained as a result of the oxidative addition.

The palladium catalyst can be stabilised in solution by adding phosphine ligands (other electron-donating ligands are used for this purpose more rarely). However, the acid halides RCOX cannot be obtained from RX and CO when the reacion is catalysed by phosphine complexes of palladium, because the oxidative addition of RX and the subsequent carbonylation of the resulting $RPd(PR'_3)_2X$ leads to the stable acyl derivative $RCOPd(PR'_3)_2X$,[17] which is incapable of reductive elimination. It was found that such acyl complexes readily react with certain nucleophiles. Thus the reaction with the alcohols R″OH yields the esters RCO_2R''.[48,54] This makes it possible to realise the catalytic cycle and to achieve the conversion of the halogeno-derivatives RX into the esters RCO_2R'' under the conditions of homogeneous catalysis by phosphine complexes of palladium:

$$RX + PdL_n \rightarrow RPdL_2X + (n-2)L,$$
$$RPdL_2X + CO \rightarrow RCOPdL_2X,$$
$$RCOPdL_2X + R''OH \rightarrow RCO_2R'' + HPdL_2X,$$
$$HPdL_2X + (n-2)L \rightarrow HX + PdL_n,$$
$$HX + B: \rightarrow BHX.$$
$$L = Pr'_3 \text{ and/or CO and B: } = \text{base}$$

The scheme presented reflects the generally accepted treatment of the mechanism of the alkoxycarbonylation of organic halides.[17,55] However, it is noteworthy that the available literature data do not rule out an alternative version of the mechanism of this reaction postulating the involvement in the catalytic cycle of the alkoxycarbonyl and not acyl complexes of palladium:[44]

$$RX + L_nPdCO \rightarrow RPd(CO)LX + (n-1)L,$$
$$RPd(CO)LX + R''OH + B: + L \rightarrow RPd(CO_2R'')L_2 + BHX,$$
$$RPd(CO_2R'')L_2 + CO + (n-2)L \rightarrow RCO_2R'' + L_nPdCO\ .$$

During the alkoxycarbonylation of RX, the strong acid HX accumulates and can cause the protolysis of the intermediate σ-organopalladium compounds[54] and may thereby exert an inhibiting effect on the course of the reaction. Organic or inorganic bases, among which tertiary amines,[44,47] potassium carbonate[56] and sodium acetates,[47] have found the most extensive application, are usually employed to remove the HX. One cannot rule out the possibility that the role of the base is also manifested in the reactivation of the nucleophile:[48]

$$R''OH + B: \rightleftarrows R''O^- + BH^+.$$

Aromatic halides are most often used as the initial substrates in the alkoxycarbonylation reaction, for example:[44]

$$ArX + BuOH \xrightarrow[100°C,\ Bu_3N]{1.5\%\ «Pd»,\ 1\ atm\ CO} \underset{46-96\%}{ArCO_2Bu}$$

X=Br, I; Ar=4-YC_6H_4 (Y=H, MeO, MeO_2C, NC), 2,6-$Me_2C_6H_3$, 1-naphthyl

The triphenylphosphine complexes of palladium $PdX_2(PPh_3)_2$ and $PhPd(PPh_3)_3X$ are effective catalysts of the process. In the case of aryl iodides, which are more reactive in oxidative addition than bromides, the reaction proceeds smoothly in the presence of palladium acetate (apparently Bu_3N plays the role of the weak stabilising ligand in this instance).

The reactivity of the halides depends on the structure of the allyl group and decreases in the sequence 4-NCC_6H_4Br > PhBr > 4-$MeOC_6H_4Br$ in the ratio 275:1:0.23 (the method of competing reactions). Judging from the half-life in the carbonylation reaction, iodobenzene is only slightly more reactive than bromobenzene. This probably shows that the oxidative addition is not the rate-limiting stage of the process.[44]† It is of interest that the steric hindrance generated by the *ortho*-substituents in 1-iodo-2,6-dimethylbenzene does not prevent the reaction: 2,6-$Me_2C_6H_3CO_2Bu$ was obtained in 63% yield.[44]

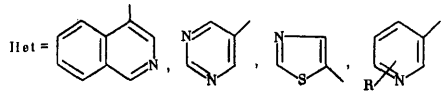
†According to Fauvarque et al.,[39] the reactivity of aryl bromides in the oxidative addition to zerovalent palladium is significantly lower than that of the corresponding iodides.

The methoxycarbonylation of aryl halides can be achieved successfully only at an elevated pressure: methyl benzoate is synthesised by the reaction of iodobenzene with methanol and CO at 3–14 atm.[47,56] Under milder conditions, (18 °C, 1 atm CO) the carbonylation takes place with a low yield.[48]

It has recently been possible to extend the reaction to heterocyclic halogenoderivatives.[57] The ethyl esters of isoquinoline-4-carboxylic, pyrimidine-5-carboxylic, and thiazole-5-carboxylic acids as well as those of substituted pyridine-carboxylic acids have been obtained in high yields:

$$\text{HetX} + \text{EtOH} \xrightarrow[100^\circ\text{C},\ Et_3N]{PdCl_2(PPh_3)_2,\ 7\ \text{atm CO}} \text{HetCO}_2\text{Et}$$

X = Br, Cl; 35–100%

Het = 

The tin and sodium alkoxides Et_3SnOMe and NaOMe can be used conveniently as the coreactant in the alkoxycarbonylation reactions of aryl iodides instead of alcohols:[58–60]

$$\text{ArI} + \underset{\text{or}\ \text{NaOMe}}{Et_3SnOMe} \xrightarrow[20^\circ C]{2\%\ PhPd(PPh_3)_2I,\ 1\ \text{atm CO}} \underset{75-99\%}{ArCO_2Me}\ .$$

Ar = 4-XC_6H_4 (X = H, MeO_2C, NC, NO_2), 1-naphthyl

The use of such powerful nucleophiles made it possible to convert ArI into $ArCO_2Me$ not only under very mild conditions but also at a high rate. Thus the carbonylation of 1-iodonaphthalene in the presence if NaOMe terminates after 4 h and leads to 1 $MeO_2CC_{10}H_7$ in 90% yield,[60] while that analogous reaction of 1-bromonaphthalene with $BuOH/Bu_3N$ does not go to completion even after 80 h: 46% of 1-$MeO_2CC_{10}H_7$; degree of conversion of 1-$C_{10}H_7Br$ 81%.[44]

The alkoxy-derivatives of aluminium,[61] boron,[62] titanium, and zirconium[63] are less reactive in the reactions with aryl halides and CO. The carbonylation in the $ArBr-E(OR)_n$ system can be achieved only at an elevated temperature in the presence of a zerovalent palladium complex (E = Ti) or a mixed catalyst containing zerovalent palladium and rhodium(I) complexes (E = Al, B, or Zr):

$$\text{ArBr} + \text{E(OR)}_n \xrightarrow[75-150\ ^\circ C]{\text{cat., 1 atm CO}} \underset{40-98\%}{ArCO_2R}$$

E = Al, B(n = 3); Ti, Zr (n = 4); cat. = 6% $Pd(PPh_3)_4$ or 6–8% $Pd(PPh_3)_4$ + 9–11% [(hexa-1,5-diene)RHCl]$_2$

Ar = XC_6H_4 (X = H, 4-MeO, 4-CH_2=CH, 3-Me), 1-naphthyl

R = Et, Pr, iso-Pr, Bu, t-Bu

Vinyl iodides and bromides interact with CO and ROH to form the esters of αβ-unsaturated carboxylic acids (1–87 atm, 60–125 °C):[44]

$$RR'C{=}CR''Y + BuOH \xrightarrow[Bu_3N]{1.5\%\ «Pd»,\ CO} \underset{58-95\%}{RR'C{=}CR''CO_2Bu}\ .$$

X=Br, I; «Pd»=$PdX_2(PPh_3)_2$

A mixture of geometrical isomers is usually obtained in which the product with retention of the configuration predominates. A decrease of temperature to 60–80 °C and the addition of an excess of triphenylphosphine make it possible to increase the stereoselectivity of the process, but the rate of carbonylation then falls markedly. Together with *cis-trans* isomerisation, the formation of side products is observed in some cases as a result of the migration of the double bond in the ester from the αβ- to the βγ-position.

The carbonylation of vinyl bromides in the presence of sodium, aluminium, boron, titanium, and zirconium alkoxides has been described only for individual examples.[59–63] The limited amount of experimental data precludes definite conclusions about the synthetic possibilities of these reactions.

The alkoxycarbonylation of allyl halides has been studied inadequately. The reaction is carried out in the presence of palladium catalysts not containing phosphine ligands under severe conditions (97–500 atm, 80–160 °C), which led to low yields of βγ-unsaturated carboxylic acid esters (29–52%).[41–43]

The methyl and butyl esters of phenylacetic acid were obtained in satisfactory yields by the carbonylation of $PhCH_2Cl$[47] or $PhCH_2Br$[56] catalysed by $PdCl_2(PPh_3)_2$. The reactions of benzyl halides can be complicated by the formation of side products as a result of the substitution of the halogen by the alkoxy-group, while in the case of substrates of the type ArCH(Alk)Hal, containing a hydrogen atom in the β-position in the alkyl chain, unsaturated compounds can be produced. Thus the carbonylation of α-bromoethylbenzene in the presence of methanol leads to methyl 2-phenylpropionate (49%), α-methoxyethylbenzene (24%), and styrene (12%).[64]

The interaction of propargyl chloride with CO in methanol is accompanied by the hydromethoxycarbonylation of the triple bond and affords methyl itaconate $CH_2=C(CO_2Me)CH_2CO_2Me$ in 66% yield.[65]

Yet another type of halide used as the initial substrates in the synthesis of esters comprises α-halogenoketones. Thus the synthesis of $PhCOCH_2CO_2Me$ (64%) by the reaction of $PhCOCH_2Br$ with CO in methanol has been described.[47]

The alkoxycarbonylation of halogeno-derivatives of saturated hydrocarbons (primary bromoalkanes) and also of phenylethyl bromide whose reactivity is similar to theirs has been achieved only recently[62,63] (1 atm CO, 90–150 °C):

$$\text{RBr} + \text{E(OBu)}_n \xrightarrow{\text{cat., CO}} \underset{42-88\%}{RCO_2Bu}\ .$$

E = B (n = 3), Ti (n = 4); R = n-C_8H_{17}, n-$C_{12}H_{25}$, $PhCH_2CH_2$

cat. = 6% $Pd(PPh_3)_4$ (E = Ti) or 6% $Pd(PPh_3)_4$ + 9% [(hexa-1,5-diene)RhCl]$_2$ (E = B)

The diester $BuO_2C(CH_2)_6CO_2Bu$ (76%) is formed in the analogous reaction of $Br(CH_2)_6Br$ with $B(OBu)_3$.[62]

At high CO pressures, double carbonylation of organic halides can take place, which is of great interest as a method of synthesis of derivatives of α-ketoacids (150 atm CO, 15–120 °C):[66]

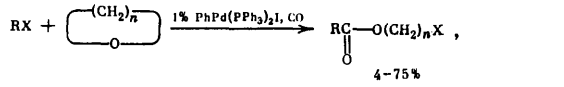
$$RX + R'OH \xrightarrow[Et_3N]{1\%\ «Pd»,\ CO} \underset{0-62\%}{RCOCO_2R'} + \underset{3-95\%}{RCO_2R'}\ .$$

RX=PhI, PhBr, 4-MeC_6H_4I, 4-$MeOC_6H_4I$, 2-iodothiophen, 5-bromothiazole, (*E*)-PhCH=CHBr

Under these conditions, the interaction of the halides RX with CO in alcohols leads to a mixture of the esters RCO_2R' and $RCOCO_2R'$, the mole fraction of the latter ranging from 0 to 91% depending on the nature of the initial reactants, the catalysts, and other factors. In order to increase the yield of α-ketoacid esters, it is essential to use as catalysts the complexes $PdCl_2L_2$, where L is the phosphine ligand with a conical angle of 145–170 °C (for example, Ph_3P, iso-Pr_3P, etc. and the process must be carried out at high pressures and low temperatures. It is recommended that the alcohols R'OH with R' = Bu, t-$BuCH_2$, iso-Pr, or cyclo-C_6H_{11} be used; when R' = Me, t-Bu, Ph, or $PhCH_2$, the only reaction product is RCO_2R'.

The ester $RCH(CO_2Et)CH_2CCl_3$ (29–60%) has been obtained together with CCl_4, RCH=CH, and CO in ethanol together with the products of the addition of carbon tetrachloride to the double bond of the initial alkene $RCHClCH_2CCl_3$ (16–33%).[67] It is not possible to extend this method to other organic halides.

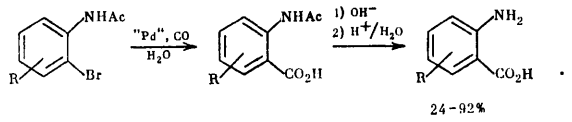
It has been proposed[68] that cyclic ethers, namely epoxides, oxetan, THF, and tetrahydropyran, be used as nucleophilic coreactants in the alkoxycarbonylation reaction (20 atm CO, 120–130 °C):



RX = PhI, PhBr, 4-AcC_6H_4Br, PhCH=CHBr, PhCH=$CHCH_2Cl$, $PhCH_2Cl$, $PhCOCH_2Cl$; $n = 2-5$

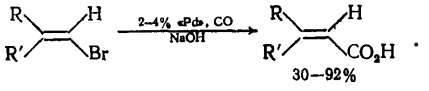
On passing from epoxides to less strained oxygen-containing heterocycles, the rate of carbonylation and the yield of products (esters of halogenohydrins) decrease sharply: oxiran > oxetan > THF > tetrahydropyran. The reactivity of tetrahydropyran does not differ from that of the acyclic dibutyl ether and the compound is almost inactive in this reaction.

The carbonylation of organic halides under the conditions of homogenous catalysis by palladium complexes is used widely in the synthesis of a wide variety of carboxylic acids. Thus the reaction of aryl halides (substituted bromobenzenes and 1- and 2-bromonaphthalenes) with CO(2–3 atm) and H_2O at 110–130 °C in the presence of the base Bu_3N and catalytic amounts of $PdX_2(PPh_3)_2$ (X = Cl or Br) or $Pd(PPh_3)_4$ leads to $ArCO_2H$ in a yield up to 94%.[69] The authors used the method to obtain anthranilic acids:



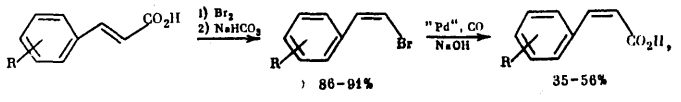
24–92%

The carboxylation of RX has been achieved[70-75] in a two-phase system: an aqueous solution of sodium hydroxide–organic solvent (C_6H_6, *p*-$Me_2C_6H_4$, CH_2Cl_2, or $EtCMe_2OH$). Tetrabutylammonium iodide,[70] tetrahexylammonium bisulphate,[72,74] benzyltriethylammonium chloride,[73,75] etc. were used as the phase transfer catalysts. We may note that the presence of a quatenary ammonium salt is not obligatory, at least in reactions with participation of benzyl halides.[72] Depending on the structurre of the halogeno-derivative RX, the following reactivity series were observed: $PhCH_2X$ > PhX and RI > RBr > RCl.[71] The carboxylation in a two-phase system usually takes place under very mild conditions. This is especially important in the reactions of halides of the vinyl type, because it makes it possible to convert them into αβ-unsaturated acids with the retention of both (*E*)- and (*Z*)-configurations of the vinyl group (1 atm CO, 20–50 °C):[73,75]



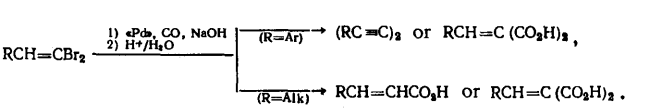
«Pd»=$Pd(PPh_3)_4$, $Pd(Ph_2PCH_2CH_2PPh_2)$;
R, R′=H, Ar, Alk

A convenient method of synthesis of *cis*-cinnamic acids from the corresponding *trans*-isomers is based on this reaction (1 atm CO, 20 °C):[73]

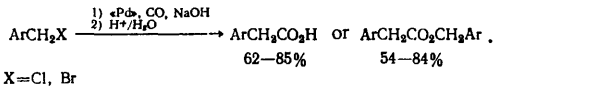


86–91% 35–56%

Depending on the nature of the initial dibromide the organic solvent employed, the interaction of 1,1dibromoalk-1-enes with CO leads to different products–diynes, αβ-unsaturated monoacids, or methylenemalonic acids (1 atm CO, 40–75 °C):[74]

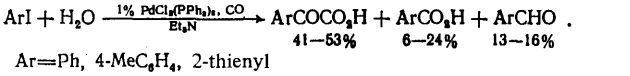


The carbonylation of benzyl halides in an aqueous sodium hydroxide solution–organic solvent system (1–5 atm CO, 20 to 95 °C) is used to synthesise arylacetic acids[70-72] and their benzyl esters.[72] The reaction pathway is determined mainly by the nature of the palladium catalyst and by the presence or absence of a quaternary ammonium salt (phase transfer catalyst):



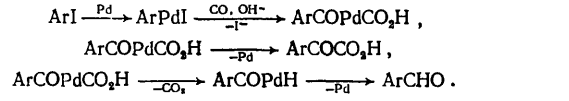
X=Cl, Br

It is noteworthy that the product of the double carbonylation of the initial halides, namely $ArCOCO_2H$, as well as a small amount of the aldehyde ArCHO are obtained together with $ArCO_2H$ from aryl iodides and H_2O at a high CO pressure (150 atm CO, 40–80 °C):[76]

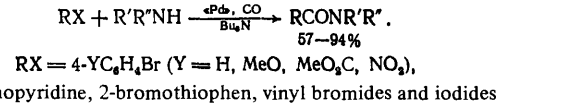


Ar=Ph, 4-MeC_6H_4, 2-thienyl

The mechanism of the formaion of the α-ketoacid and the aldehyde proposed by the authors is presented in the Scheme below (the ligands not involved in the reaction have been omitted from the Scheme):



The interaction of the halides RX with CO and the amines R′R″NH (1 atm, 100 °C), catalysed by 1.5 mole% of $PdX_2(PPh_3)_2$, leads to the carboxylic acid amides RCONR′R″.[45] Halogeno-derivatives of the aryl and vinyl types can be used as the initial substrates in the reaction. The amine base (Bu_3N) is as a rule added to neutralise, together with the amine reactant (R′R″NH), the acid HX evolved in the carbonylation reaction:



RX = 4-YC_6H_4Br (Y = H, MeO, MeO_2C, NO_2),
3-bromopyridine, 2-bromothiophen, vinyl bromides and iodides
R′R″NH=$PhNH_2$, $PhCH_2NH_2$, $(CH_2)_4NH$

The conversion of organic halides into amides is achieved at a higher rate than that of the analogous alkoxycarbonylation reaction. For example, the amide $PhCONHCH_2Ph$ is formed 17 times faster in the reaction of PhBr with CO and $PhCH_2NH_2$ than the ester $PhCO_2Bu$ in the carbonylation of PhBr in the presence of BuOH.[45] It may be that this difference between the rates is the reason why the conversion of vinyl iodides and bromides into amides proceeds with complete retention of the configuration of the alkenyl group[45] in contrast to the alkoxycarbonylation of these compounds.[44]

It has been shown[60] that Me_3SnEt_3 reacts with ArI (Ar = Ph or 4-$NO_2C_6H_4$) and CO under very mild conditions (20 °C, 1 atm) with formation of $ArCONEt_2$ (82–90%). When the organo-tin nucleophile is replaced by the corresponding amine (Et_2NH), both the selectivity and the rate of the amide formation reaction decrease sharply.

Initially two fundamentally different mechanisms were proposed for the conversion of organic halides into amides in the presence of palladium catalysts[45] the acyl ($RCOPdL_2X$) or carbamoyl [$RPd(CONR'R'')L$] complexes of palladium were initially considered as intermediates (cf. with the alkoxycarbonylation mechanism described above). The experimental data obtained in later studies[59,60,77] showed that the reaction apparently takes place via the second pathway, i.e. the catalytic cycle in which the carbamoyl complexes participate is realised:

$$RX + PdL_n \rightarrow RPdL_2X + (n-2)L,$$
$$RPdL_2X + CO \rightleftarrows [RPd(CO)L_2]^+X^-,$$
$$[RPd(CO)L_2]^+X^- + R'R''NH + B: \rightarrow RPd(CONR'R'')L_2 + BHX,$$
$$RPd(CONR'R'')L_2 + (n-2)L \rightarrow RCONR'R'' + PdL_n,$$
$$L = PR_3 \text{ and/or } CO$$

Under certain conditions the reactions of organic halides with CO in the presence of primary or secondary amines lead to double carbonylation products – α-ketoacid amides (10 – 40 atm CO, 20 – 100 °C):[78,79]

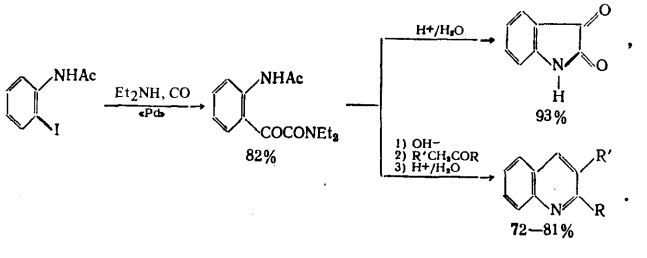
$$RX + R'R''NH \xrightarrow[\text{«Pd»}, CO]{0.5-1\%} \underset{0-98\%}{RCOCONR'R''} + \underset{2-92\%}{RCONR'R''}.$$

X=Br, I; R=4-YC_6H_4 (Y=H, Me, MeO, Cl), 2-thienyl, 3-pyridyl, PhCH = CH

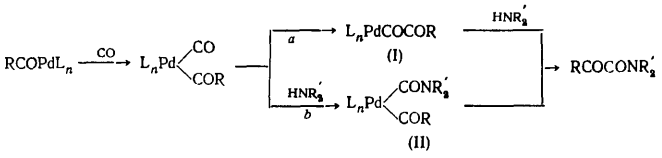
R'=R''=Me, Et, Pr, iso-Pr; R'R''= $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

The overall yield of the mixture of acid amides is 3 – 100%. The molar ratio RCOCONR'R''/RCONR'R'' varies within wide limits (0/100 – 98/2) and depends on a number of parameters. The formation of the α-ketoamide is promoted by the increase in the CO pressure, the decrease in the reaction temperature, the use of non-polar solvents.[78,80] The nature of the catalyst – a phosphinepalladium complex – plays a major role.[78] In the case of complexes with monodentate ligands – PdX_2L_2 and $PhPdL_2X$ – the relative content of RCOCONR'R'' in the mixture of products increases with increasing basicity of the phosphine L: $Me_2PhP > EtPh_2P > Ph_3P$. When the complexes PdU_2L, where L is a bidentate ligand of the type $Ph_2P(CH_2)_nPPh_2$, are used as the catalysts, the reaction selectivity calculated relative to RCOCONR'R'' diminishes as a function of *n* in the sequence 4 > 3 > 5 > 2. α-Ketoacid amides are obtained in high yields when RX is carbonylated in the presence of Et_2NH, Pr_2NH, or piperidine.[78-80] The reactions with weaker bases, namely Me_2NH and morpholine, and also with the sterically hindered iso-Pr_2NH afford mainly the monocarbonylation products.[78-80]

The method of synthesis of isatin and quinoline derivatives, proposed by Ozawa et al.,[81] is based on the double carbonylation of *o*-iodoacetanilide:



The acylpalladium complexes $RCOPdL_n$ (L = X, PR'_3 and/or CO), formed as a result of the oxidative addition of RX to zero-valent palladium and the subsequent interaction of $RPdL_n$ with CO, are undoubtedly active intermediates in the double carbonylation reactions considered. The conversion of $RCOPdL_n$ into α-ketoamides of carboxylic acids can be achieved in principle via two different mechanisms:[79,80] via the stage involving the formation of the acylformyl derivative of palladium (I) or of the acylcarbamoyl complex (II):



On the basis of a careful study of the reactions of the palladium complexes $RPdL_2X$, $RCOPdL_2X$, and $RCOCOPdL_2X$ (L = phosphine ligands), modelling the possible pathways in the catalytic process, it has been recently possible[77,82-84] to demonstrate that the double carbonylation of organic halides proceeds with participation of compounds (II) (pathway *b*).

It is of interest that not only primary and secondary but also tertiary amines can be used as the nucleophilic coreactants in the conversion of the halogeno-derivatives RX into amides (20 atm CO, 120 °C):[85]

$$RX + R'_2R''N \xrightarrow[CO]{0.6\%\ PhPd(PPh_3)_2I} \underset{11-75\%}{RCONR'R''} + R'X.$$

RX=PhI, PhCH=CHBr, EtI

R'=R''=Et, Pr, Bu; R'=Et, R''=Ph

On passing from triethylamine to tripropyl- and tributyl-amines, which contain more bulky substituents, the yield of RCONR'R'' falls significantly. The fact that the carbonylation of EtI in the presence of $PhNEt_2$ proceeds with the selective dissociation of the N – Et bond and affords the *N*-ethyl-*N*-phenylamide of propionic acid in a high yield (75%) is noteworthy.

Non-activated iodoarenes and iodoarenes containing weak electron-accepting substituents interact with CO and organo-tin mercaptides to form thiolocarboxylic acid esters (1 atm CO, 20 °C):[58,59]

$$ArI + Et_3SnSR \xrightarrow[CO]{5-10\%\ PhPd(PPh_3)_2I} \underset{62-96\%}{ArCOSR}.$$

Ar=Ph, 4-ClC_6H_4, 1-naphthyl, 2-thienyl; R = Ph, Et

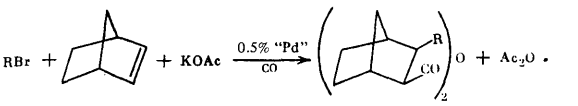
When the initial halide contains strong electron-accepting groups, ArCOSR cannot be obtained; the main reacion product is in this case the sulphide ArSR.

Aryl iodides have been converted into α-ketonitriles[86] (8 – 20 atm CO, 100 °C:

$$ArI + KCN \xrightarrow[CO]{1-3\%\ PhPd(PPh_3)_2I} \underset{45-92\%}{ArCOCN} + \underset{1-22\%}{ArCN},$$

Ar=4-XC_6H_4 (X=H, Me, MeO), 2-thienyl.

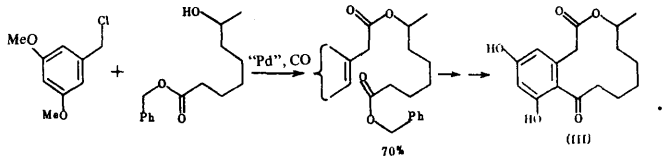
The carbonylation in the RBr – KOAc – norbornene (or norbornadiene) system, catalysed by tetrakis(triphenylphosphine)palladium, is accompanied by the insertion of both the alkene and CO in the C – Pd bond in the intermediate $RPd(PPh_3)_2Br$ (1 atm CO, 80 °C):[87]



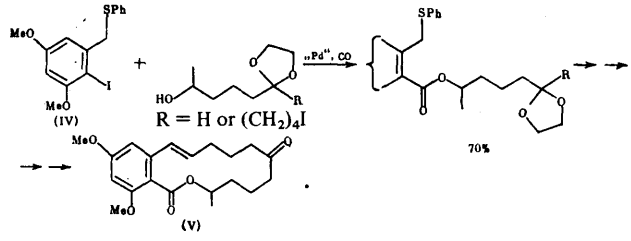
R = Ph, $PhCH_2$, MeO_2CCH_2, PhCH=CH, n-$C_6H_{13}CH$ = CH

A mixed anhydride is apparently formed initially, but it is unstable and readily disproportionates. The reactions considered above have found application in fine organic synthesis.

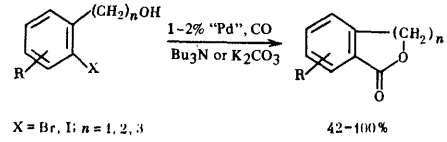
A method of synthesis of the macrolide(III) (curvularin), which is encountered in nature, has been developed. The key stage is the alkoxycarbonylation of 3,5-dimethoxybenzyl chloride:[88]



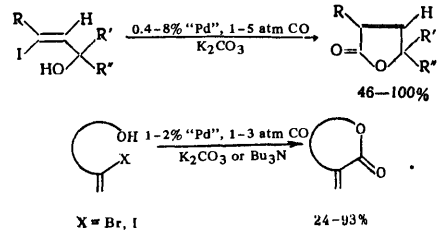
The dimethyl ether of zearalenone (V), a macrolide with a structure similar to that of curvularin, has been synthesised from the aryl iodide (IV) using a catalytic reaction:[89,90]



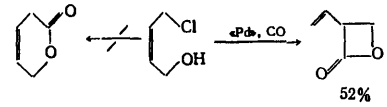
Hitherto, we have discussed the interaction of organic halides with CO and a wide variety of nucleophilic coreactants without dealing with the carbonylation of substrates containing a nucleophilic substituent (OH, NH_2, etc.) in the same molecule. On the other hand, the reactions of such halogenoderivatives with CO are of special interest from the synthetic point of view, because, unless this is prohibited by geometrical considerations, the latter can occur as intramolecular reactions leading to various heterocyclic compounds. For example, in the presence of an OH grup in the side chain of halogenobenzene, cyclisation takes place readily with formation of benzolactones (1–4 atm CO, 50–130 °C).[56,91] Special mention should be made of the possibility of obtaining in this way derivatives of the phthalide (n = 1) and 3,4-dihydroisocoumarin (n = 2) series, many of which are encountered in natural objects and exhibit biological activity:[35]



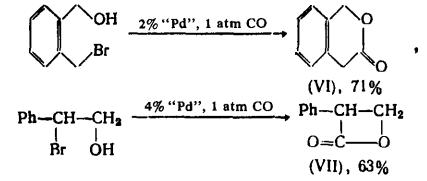
The reactions of vinyl halides, containing a hydroxy-group, have been used successfully for the synthesis of compounds of important classes such as $\Delta^{\alpha\beta}$-butenolides[56] and α-methylene-substituted γ-, δ-, and ε-lactones:[92,93]



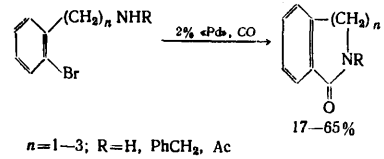
It has been found[56] that a chloro-derivative of the allylic type—*cis*-4-chlorobut-2-en-1-ol—interacts with CO under very mild conditions (1 atm, 20 °C) in the presence of 4 mole% of $Pd(CO)(PPh_3)_3$ as the catalyst. The reaction leads to a four-membered ring lactone:



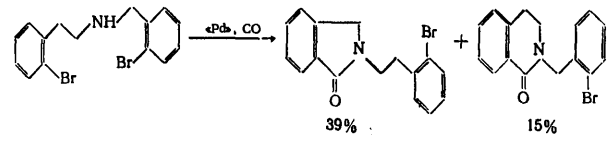
o-Bromomethylbenzyl alcohol and 2-bromo-2-phenylethanol react to form 3-isochromanone (VI) and the β-lactone of tropic acid (VII) respectively in satisfactory yields:[56]



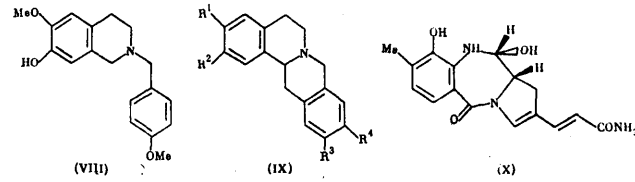
The conversion of *o*-(aminoalkyl)bromobenzenes into γ-, δ-, and ε-benzolactams hs been achieved[94,95] (1 atm CO, 100 °C):



When the intramolecular cyclisation can proceed via different pathways affording both six- and five-membered lactams, the latter is formed preferentially:[94]

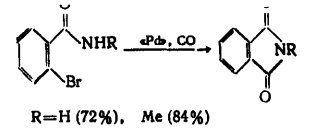


The simplest alkaloids (VIII) and (IX), whose composition includes the tetrahydroisoquinoline system, have been synthesised using this elegant and convenient method for the construction of nitrogen-containing rings:[96,97]



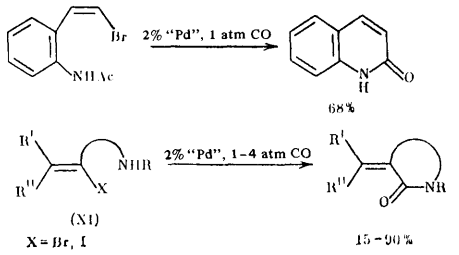
Recently there has been a growth of interest in benzo-1,4-diazepines and their oxo-derivatives, among which substances active as tranquillisers, soporifics, and antibiotics have been discovered. A method has been developed for the synthesis of a series of physiologically active 1,4-benzodiazepines based on the cyclisation reaction catalysed by palladium complexes. One of the antibiotics synthesised in this way is anthramycin (X).[99]

o-Bromobenzamides interact with CO at 1 atm and 100 °C in the presence of the $Pd(OAc)_2$–PPh_3 catalytic system with formation of phthalimides:[95]



Vinyl halides are also used as the initial substrates in the synthesis of nitrogen-containing heterocyclic compounds. Thus the conversion of (*Z*)-*o*-acetamido-β-bromostyrene into 2-quinolone can be

readily achieved.[95] The carbonylation of the vinyl derivatives (XI) leads to a wide variety of the substituted α-methylene-β-lactams, α-methylene-γ-lactams, and α-methylene-δ-lactams:[93,103,104]



The possible applications of this method in the synthesis of β-lactam antibiotics are being sought.[105]

2. The Synthesis of Aldehydes

The halogen in organic halides can be readily replaced by the formyl group using the carbonylation reaction.

In the presence of the synthesis gas ($CO:H_2$ = 1:1) and a palladium catalyst, iodo- and bromo-arenes of the benzene and heterocyclic series as well as vinyl derivatives are converted into the corresponding aldehydes in satisfactory yields.[46,106] The reaction takes place at approximately 100 atm and 80–150 °C in the presence of a base (a tertiary amine or pyridine):

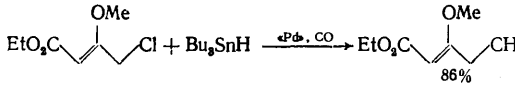
$$RX + CO + H_2 \xrightarrow[65-99\%]{1-3\%\ «Pd»} RCHO\ .$$

«Pd»=PdX_2, $PdX_2(PPh_3)_2$; X=Br, I; R=Ar, vinyl.

In the case of vinyl halides, side products may be formed as a result of *cis–trans* isomerisation and the migration of the double bond. Substituents in halogenoarenes such as the cyano- and acetoxy-groups are not involved in the reaction. However, when an attempt was made to obtain *p*-nitrobenzaldehyde by formylating *p*-bromonitrobenzene, only polymeric products were isolated. In certain cases the reduction of the carbon–halogen bond is observed. Thus, the reaction of *o*-dibromobenzene leads to benzaldehyde (66%). However, in the reaction involving *p*-dibromobenzene, the normal product *p*-$(HCO)_2$.C_6H_4 with two aldehyde groups was obtained (74%).

The mechanism of the formylation of RX is in many respects analogous to the mechanisms of the reactions examined before: the active intermediate is the acyl complex of palladium $RCOPdL_2X$, the interaction of which with H_2 leads to the aldehyde RCHO.[46]

The use of tributyl-tin hydride as the reductant made it possible to convert organic halides into aldehydes under much milder conditions (1–3 atm CO, 50 °C).[107] Apart from aryl and vinyl iodides, allyl chlorides and benzyl bromide can serve as the initial substrate:



$$PhCH_2Br + Bu_3SnH \xrightarrow[75\%\ \ 12\%]{«Pd»,\ CO} PhCH_2CHO + PhMe\ .$$

«Pd»=$Pd(PPh_3)_4$

Formylation by the method of Baillargeon and Stille[107] is more chemoselective than the analogous reaction using synthesis gas: the methoxycarbonyl, keto-, and even nitro-groups are not involved in the reaction. In the reaction of *p*-bromoiodobenzene it is possible to achieve the selective substitution of iodine by the formyl group; the yield of *p*-bromobenzaldehyde reaches 88%. The formation of aldehyde is sometimes complicated by a side reaction involving the reduction of the initial halogeno-derivative RX to RH. For halogenoarenes containing strong electron-accepting substituents, this reaction may become the main one. For example, the formylation of *p*-$NO_2C_6H_4I$ leads to *p*-nitrobenzaldehyde (38%) and nitrobenzene (62%). Nevertheless, the yield of the aldehyde is usually high and in many cases reaches 90–100%.

Pri-Bar and Buchman[108] were able to replace tin hydride, which is sensitive to atmospheric oxygen, by the mild reductant poly(methylhydrosiloxane):

$$RX + [-SiMeH-O-]_n \xrightarrow[80-125°C]{«Pd»,\ 3\ atm\ CO} \underset{14-96\%}{RCHO}\ .$$

"Pd" = $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$/polystyrene

RX = iodo- and bromo-arenes and benzyl bromide

$PdCl_2(PPh_3)_2$ deposited on cross-linked polystyrene is an effective catalyst. The immobilisaion of the palladium complex on a polymeric carrier made it possible, on the one hand, to retain the activity characteristic of the homogeneous catalyst and, on the other hand, to simplify significantly the problem of the separation of the palladium compounds from the reaction products.

The possibility of using HCOONa as the reductant in the formylation reaction (3 atm CO, 125 °C) has been demonstrated for iodo- and bromo-benzenes.[108] The yield of benzaldehyde was 80% and 58% respectively.

3. The Synthesis of Asymmetric Ketones

Carbonylation in the RX (organic halide)–R'M (organometallic compound) system, catalysed by palladium complexes, constitutes a convenient method of synthesis of asymmetric ketones:

$$RX + R'M \xrightarrow{«Pd»,\ CO} RCOR' + MX\ .$$

The reaction mechanism is in broad outline analogous to the mechanisms of the reactions considered in this Section. The first stage of the catalytic cycle is the oxidative addition of RX to the zerovalent palladium complex. The carbonylation of the $RPdL_2X$ formed and the subsequent interaction of the acyl derivative $RCOPdL_2X$ with R'M lead to the ketone RCOR' and the initial catalytically active zerovalent palladium species.

Tin derivatives have found the widest application as organometallic reagents in this reaction. They are resistant to the action of atmospheric oxygen and moisture, are readily available, and, what is most important, are inert not only in relation to the keto-group of the products COR' but virtually in relation to any important functional group. This permits the synthesis of ketones containing different substituents.

The carbonylation of the iodoarenes 4-XC_6H_4I in the presence of aryl-, vinyl-, phenylethynyl-, and alkyl-stannanes leads to the corresponding ketones in high yields (1–30 atm CO, 20–120 °C):[109,110]

$$4\text{-}XC_6H_4I + RSnR'_3 \xrightarrow[HMP]{«Pd»,\ CO} 4\text{-}XC_6H_4COR + ISnR'_3\ ,$$

X=H, Cl, MeO_2C, CN, NO_2; R=4-YC_6H_4 (Y=MeO, Me, H, Cl, NO_2), C_6F_5, 2-thienyl, H_2C=CH, PhC≡C, Me, Bu

"Pd" = $PhPd(PPh_3)_2I$, $(\pi\text{-}C_3H_5PdCl)_2$

The reaction takes place under very mild conditions (1 atm CO, 20 °C) when it is catalysed by bis(π-allylpalladium chloride) (1 mole%).[110] In the reactions involving the most active tin compounds $RSnMe_3$ (R=CH_2=CH, 2-thienyl, or PhC≡C), the cross-coupling side product 4-XC_6H_4R is formed together with the carbonylation product. This undesirable process can be suppressed by carrying out the reaction in a less polar solvent–acetone.[111]

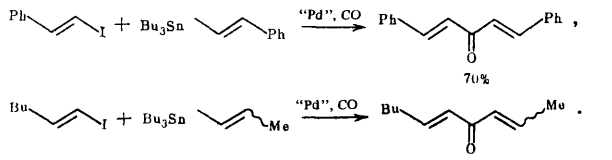
The halides of the heterocyclic series react analogously. Thus 2-C_4H_3SCOPh (95%) and 2-C_5H_4NCOPh (91%) have been obtained by carbonylating 2-iodothiophen and 2-iodopyridine in the presence of trimethylphenyltin.[111]

The reactions of β-bromostyrene with tetramethyltin,[109] of 1-iodohex-1-ene with tributylphenyltin, and of 1-iodopent-1-ene with $PrC{\equiv}CSnBu_3$ [112] at 4–30 atm CO and 45–120 °C lead to the corresponding αβ-unsaturated ketones in 46–62% yields. A method of synthesis of asymmetric divinyl ketones from vinyl iodides and alkenyltin derivatives (4 atm CO, 45–50 °C) has been developed:[112]

$$R^1R^2C{=}CR^3I + R^4R^5C{=}CHSnAlk_3 \xrightarrow{2\%\ «Pd»,\ CO} \rightarrow Alk_3SnI + R^1R^2C{=}CR^3CCH{=}CR^4R^5 \ (O;\ 45–93\%)$$

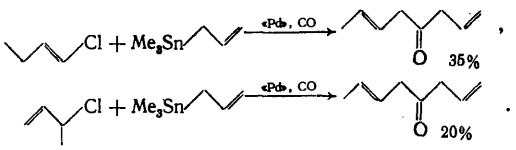
«Pd» = $PdCl_2L_2$, $PhCH_2PdL_2Cl$; L = PPh_3

We may note that the *trans*-configuration of the alkenyl group in the initial halide and the organostannane is retained in the reaction product. In the case of *cis*-organostannanes the carbonylation also takes place with the preferential retention of the geometry of the double bond, but the subsequent isomerisation of the ketone under the reaction conditions can lead to the *trans*-product, for example:

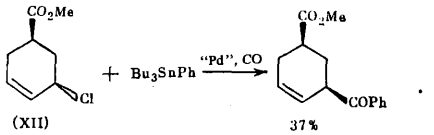


cis/*trans* = 6 24 h: *cis*/*trans* = 2.5
48 h: only *trans*-isomer, 62%

Allyl halides interact with aryl-, vinyl-, and allyl-trialkylstannanes at 4–52 atm CO with formation of βγ-unsaturated ketones.[113-115] Organotrimethylstannanes are usually employed in order to reduce the steric hindrance generated by the alkyl substituents in the organotin compound. The reactions of allyl bromides proceed less selectively than those of allyl chlorides. Although the carbonylation can be accompanied by the allylic rearrangement, it is regioselective: only one product is obtained in which the carbonyl grup is linked to the least substituted carbon atom of the allyl fragment:[114]



As shown for compound (XII), the stereochemical result of the reaction corresponds to inversion of the configuration at the carbon atom linked to the halogen:[115]



(XII) 37%

cis/*trans* = 26:74 *cis*/*trans* = 70:30

Vinylstannanes interact with allyl halides in a CO atmosphere with retention of both the *cis*- and the *trans*-geometry of the vinyl group.[115]

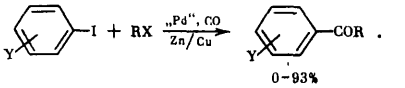
Benzyl chloride reacts with tetramethyltin and CO to form phenylacetone (86%).[109] *p*-Nitrobenzyl phenyl ketone has been obtained analogously in 85% yield from *p*-nitrobenzyl bromide and trimethylphenyltin.[110] The reaction of PhCHRBr (R = Me or Et) with R'_4Sn (R' = Me or Ph) and CO is complicated by side processes involving isomerisation and β-elimination,[116] for example:

$$PhCHMeBr + Me_4Sn \xrightarrow[120°C]{PdCl_2(AsPh_3)_2,\ 20\ atm\ CO} \rightarrow \underset{70\%}{PhCHMeCOMe} + \underset{4\%}{PhCH_2CH_2COMe} + \underset{14\%}{PhCH{=}CH_2}$$

Carbonylation in an α-halogenocarboxylic acid ester–organotin compound system constitutes a method of synthesis of β-ketoacid derivatives. Thus the reaction of ethyl α-bromoacetate with CO and tetraphenyltin leads to ethyl benzoylacetate (67%).[109] MeCH.(COMe)CO_2Et has been obtained from ethyl α-bromopropionate and tetramethyltin (62%).

The conversion of halogeno-derivatives of saturated hydrocarbons into ketones has been described for only one example: methyl iodide interacts with trimethylphenylstannane in a CO atmosphere to form acetophenone (94%).[110]

The organozinc compounds RZnX, obtained *in situ* from primary or secondary iodoalkanes or benzyl chlorides using the zinc–copper couple, react with aryl iodides at 1 atm CO in the presence of 1 to 2 mole% of $Pd(PPh_3)_4$.[117] The yield of the target product $YC_6H_4.COR$ is 56–93% for aryl iodides containing electron-donating substituents (Y = 4-MeO or 2- and 4-Me) and unsubstituted iodobenzene (Y = H), but in the presence of electron-accepting groups in the benzene ring of the halogenoarene (Y = 4-Br or 2-MeO_2C) it falls to 0–38%. It is also noteworthy that primary alkyl iodides are more reactive than secondary alkyl iodides:



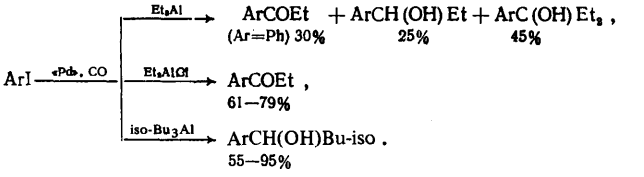
X = I; R = Me, n-Pr, iso-Pr, iso-Bu, n-C_8H_{17}, cyclo-C_6H_{11}
X = Br; R = $PhCH_2$, 4-$ClC_6H_4CH_2$

Carbonylation in the RX–iso-Bu_2AlR' system under mild conditions (1 atm CO, 20–55 °C) can serve as a convenient method of synthesis of asymmetric ketones RCOR' of various classes:[118]

$$RX + \text{iso-}Bu_2AlR' \xrightarrow{1\%\ PdCl_2(MeCN)_2,\ CO} \underset{41–99\%}{RCOR'}$$

RX = 4-YC_6H_4I (Y = NO_2, NC, Cl, MeO, H), 2-iodothiophen, 4-$NO_2C_6H_4CH_2Br$, MeI
R' = Ph, PhC≡C, CH_2=CH

The reaction of aluminium trialkyls and dialkylaluminium chlorides with aryl iodides and CO (1 atm, 50 °C) takes place in a more complex manner.[119] Alkyl aryl ketones ArCOAlk obtained initially are capable of bineg reduced and alkylated by the initial organoaluminium compounds, affording, ArCH(OH)Alk and $ArC(OH)Alk_2$. Thus the carbonylation of iodobenzene in the presence of Et_3Al leads to a mixture containing the three products indicated in comparable amounts. The use of Et_2AlCl and iso-Bu_3Al as reactants made it possible to direct the process towards the preferential formation of a ketone or secondary alcohol respectively:



The ketones RCOC≡CR' are obtained from the halides RX and terminal acetylenes R'C≡CH (R' = Ph, $PhCH_2CH_2$, or Bu) in a CO atmosphere (20 atm, 80–120 °C).[120] The method is applicable over

a wide range of organic halides: substituted iodo- and bromo-benzenes, 1-bromonaphthalene, 2-bromothiophen, and vinyl bromides. In order to increase the yield of the ketone and to reduce the amount of the side products [$RC{\equiv}CR'$, $(R'C{\equiv}C)_2$], it is recommended that the complex $PdCl_2$ with the bidentate phosphine ligand 1,1'-bis(diphenylphosphino)ferrocene be used:

$$RX + R'C{\equiv}CH \xrightarrow[Et_3N]{1\%\ «Pd»,\ CO} \underset{47-93\%}{RCOC{\equiv}CR'}\ .$$

The reactions of aryl iodides with $RC{\equiv}CH$ at 1 atm CO and approximately 60 °C in the presence of the zinc–copper couple lead mainly to the enone $ArCOCH{=}CHR$ after the hydrolysis of the reaction mixture:[121]

$$ArI + RC{\equiv}CH \xrightarrow[2)\ H_2O]{1)\ cat.,\ CO,\ Zn/Cu} \underset{33-92\%}{ArCOCH{=}CHR} + \underset{0-26\%}{ArCOCH{=}CAr}R + \underset{0-44\%}{ArCOCH_2CHRCOAr} + \underset{0-23\%}{ArC{\equiv}CR}\ .$$

cat. = 2% $PdCl_2(PPh_3)_2$ + 4% $(C_6H_5)_2TiCl_2$

R=Ph, Bu; Ar=YC_6H_4 (Y=H, Me, MeO, Br), 2-thienyl.

The $ArCOC{\equiv}CR$ formed initially is apparently reduced by Zn/Cu to $ArCOCH{=}CRZnI$ whose subsequent interaction with water affords $ArCOCH{=}CHR$.[121]

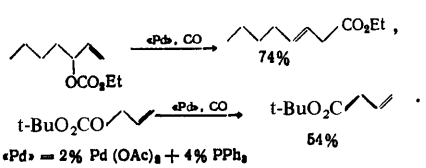
The possibility, in principle of synthesising symmetrical diaryldiketones by carbonylating aryl iodides in the presence of palladium catalysts (8 atm CO, 111 °C) has been demonstrated recently[122] for the conversion of *p*-iodoanisole into *p*-bianisoyl:

$$4\text{-}MeOC_6H_4I + Et_6Sn_2 \xrightarrow{1\%\ «Pd»,\ CO} \underset{71\%}{(4\text{-}MeOC_6H_4CO)_2} + Et_3SnI\ .$$

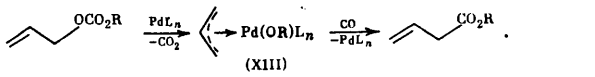
Thus the study of the reactions of organic halides with CO under the conditions of homogeneous catalysis by palladium complexes has led to the development of new convenient methods of synthesis of carboxylic acids and their derivatives, aldehydes, and symmetrical and asymmetrical ketones.

IV. CARBONYLATION OF OTHER ORGANIC SUBSTRATES

Not only organoelemental compounds and organic halides but also other substrates, capable of interacting with zerovalent palladium or palladium(II) complexes to form σ-organopalladium compounds, can serve as donors of organic groups in the carbonylation reaction. Thus, as early as the 1960's, it was shown[42,50] that ethers and esters of allyl alcohols react with CO in the presence of palladium catalysts. However, the severe conditions under which the process takes place and the low yields of the products precluded a wide-scale application of this synthetic method. Only much later was it found[123] that the readily available alkyl allyl carbonates exhibit a high reactivity: their carbonylation takes place under mild conditions (1–10 atm, 50 °C) and leads to βγ-unsaturated acid esters in satisfactory yields, for example:

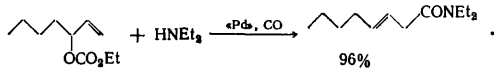


The carbonylation is regioselective: only one product is formed in which the alkoxycarbonyl group is bound to the least substituted carbon atom of the allyl fragment. π-Allyl complexes of palladium (XIII), obtained as a result of the oxidative addition of allyl carbonates to zerovalent palladium on subsequent decarboxylation, are intermediates in the reactions considered:



(XIII)

When diethylamine is introduced into the reaction mixture as a nucleophilic coreactant, amides can be synthesised:[123]

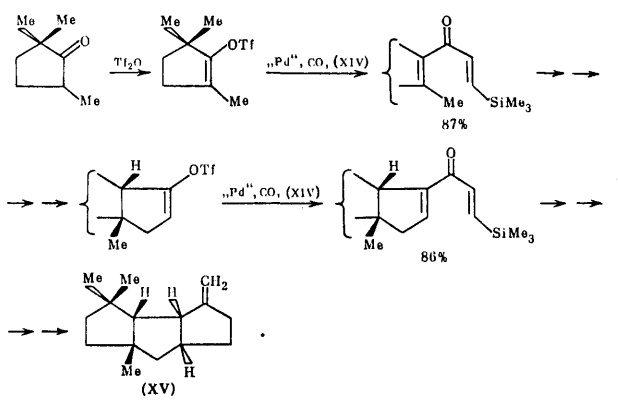


The vinyl esters of trifluoromethanesulphonic acid (vinyl triflates) interact with CO and various organotin compounds (alkyl-, aryl-, vinyl-, ethynyl-, and allyl-trialkylstannanes) to form αβ-ketones (1–4 atm CO, 20–75 °C):[124]

$$RCH{=}CR'OSO_2CF_3 + R''SnAlk_3 \xrightarrow{3\%\ Pd(PPh_3)_4,\ CO} \underset{70-95\%}{RCH{=}CR'COR''}\ .$$

It is important to note that both the (*Z*)- and (*E*)-configurations of the alkenyl group in the initial vinyl stannanes are retained in the reaction. This constitutes an undoubted advantage of the given method compared with the analogous method of synthesis based on the carbonylation of vinyl halides[112] (see above). The ready availability of vinyl triflates, the methods of synthesis of which from the anhydride of trifluoromethanesulphonic acid and the corresponding ketones have now been thoroughly developed, is also important from the preparative point of view.

There has been an interesting communication about the synthesis of compound (XV) using (*E*)-1-trimethylsilyl-2-trimethylstannylethylene (XIV) (Tf = CF_3SO_2):[124]



The carbonylation of alcohols in the presence of palladium catalysts is of very limited importance and is applicable only to allyl derivatives.[41,42,50] The reaction proceeds with low yields at high CO pressures. Homogeneous catalytic systems based on rhodium compounds proved to be much more promising. Thus, in the presence of small amounts of added HI, certain carbonyl rhodium complexes are capable of catalysing the conversion of methanol into acetic acid at relatively low CO pressures (30–40 atm) (the active substrate is not the alcohol itself but the methyl iodide formed *in situ* by the reaction of methanol with HI; the interaction of MeI with CO and H_2O leads to acetic acid with the simultaneous regeneration of HI). This highly selective reaction served as the basis of a large-scale industrial process developed by the Monsanto Company.[8]

The wide scale synthetic possibilities of the reactions involving the carbonylation of arenediazonium salts have been demonstrated.[125-128] The interaction of arenediazonium tetrafluoroborates with sodium

carboxylates at 9 atm CO and 25 °C yields mixed anhydrides of the carboxylic acids:[125,126]

$$ArN_2BF_4 + RCO_2Na \xrightarrow{1\text{–}2\%\ Pd(OAc)_2,\ CO} ArCOCR \quad (O\ O;\ 28\text{–}86\%)$$

Ar = YC_6H_4 (Y = H, Me, MeO, Cl, Br, I, NO_2), 1-naphthyl

R = H, Me, Et, t-Bu, Ph

Heating of the mixed anhydrides to 100–120 °C *in vacuo* induces their disproportionation to $(ArCO)_2O$ and $(RCO)_2O$ in nearly quantitative yields.[126] It is of interest that substituents in ArN_2BF_4 such as chlorine, bromine, and even iodine are hardly involved during the carbonylation reaction. Thus an anhydride has been obtained from *p*-iodobenzoic acid in 86% yield relative to the initial diazonium salt.[125]

The reaction of PhN_2BF_4 with CO and alcohols ROH (R = Me, Et, Bu, or t-Bu) results in the formation of $PhCO_2R$ (0–21%) and $PhCO_2H$ (7–66%).[125]

In the presence of triethylsilane or better poly(methylhydrosiloxane), CO, and a palladium catalyst, the conversion of ArN_2BF_4 into ArCHO can be readily achieved (9 atm CO, 25 °C).[127] The formation of diazonium salts is a more chemo-selective process than the analogous reaction of halogenoarenes (see Section III): chlorine, bromine, and iodine atoms and acyl, alkoxycarbonyl, and nitro-groups are not reduced under the conditions used for the synthesis of aldehydes.

Asymmetric ketones can be obtained from ArN_2X and tetra-organostannanes in a CO atmosphere (9 atm CO, 25 °C):[128]

$$YC_6H_4N_2X + R_4Sn \xrightarrow[40\text{–}90\%]{2\%\ Pd(OAc)_2,\ CO} YC_6H_4COR + R_3SnX .$$

X = BF_4, PF_6; Y = H, 2-, 3- and 4-Me, 2- and 4-Cl, 4-Br, 4-F, 3- и 4-NO_2; R = Me, Et, Ph

We may note that the possibility of using arenediazonium salts ArN_2X as the substrates in various carbonylation reactions catalysed by palladium compounds is due to the ease of formation of the σ-organopalladium complexes $ArPdL_2X$:[125]

$$ArN_2X + PdL_n \rightarrow ArPdL_2X + N_2 + (n-2)\,L.$$

Diaryliodonium halides exhibit a high reactivity in the reactions with CO. Thus the alkoxycarbonylation of $[Ar_2I]X$ and their conversion into amides proceed under extremely mild conditions (1 atm CO, 20 °C) in the presence of 2 mole% of $PdCl_2$ and lead to quantitative yields of esters and amides respectively:[129]

$$[Ar_2I]X + ROH \xrightarrow[Bu_3N]{«Pd»,\ CO} \underset{\sim 100\%}{ArCO_2R} + ArI ,$$

$$[Ar_2I]X + PhNH_2 \xrightarrow[Bu_3N]{«Pd»,\ CO} \underset{\sim 100\%}{ArCONHPh} + ArI ,$$

X = Cl, Br, I; R = Me, Bu; Ar = YC_6H_4 (Y = H, 4-MeO, 4-Me, 4-t-Bu, 4-Cl, 3-NO_2), 2,4,6-$Me_3C_6H_2$.

The steric hindrance generated by the substituents in the aromatic ring does not prevent their reaction. For example, methyl 2,4,6-trimethylbenzoate has been obtained in 100% yield.

Symmetrical diaryl ketones are formed in the presence of reductants—copper or tin powder or best of all zinc dust (1 atm CO, 20 °C):[130,131]

$$[Ar_2I]X + Zn \xrightarrow{5\%\ Pd(OAc)_2,\ CO} \underset{38\text{–}68\%}{Ar_2CO} + \underset{90\text{–}100\%}{ArI} + ZnX_2 .$$

X = Cl, Br, I, BF_4; Ar = 4-YC_6H_4 (Y = H, Me, t-Bu, Cl, Br), 2,4,6-$Me_3C_6H_2$

The main side products are α-diketones $(ArCO)_2$ (up to 24%) and biaryls Ar_2 (up to 49%). The presence of electron-donating substituents in the initial diaryliodonium salt increases and that of electron-accepting groups decreases the yield of carbonyl-containing compounds. The catalytic cycle proposed by Uchiyama et al.[131] is presented schematically below:

$$[Ar_2I]X \xrightarrow[-ArI]{Pd(0)} ArPdX \xrightarrow[-ZnX_2]{Zn} Ar_2Pd + Pd(0) ,$$

$$Ar_2Pd \xrightarrow{CO} ArCOPdAr \xrightarrow{CO} (ArCO)_2Pd$$

$$\downarrow \qquad \downarrow \qquad \downarrow$$

$$Ar_2 + Pd(0) \quad Ar_2CO + Pd(0) \quad (ArCO)_2 + Pd(0) ,$$

The metallation of arenes by palladium(II) salts affords the σ-diorganopalladium compounds ArPdX,[132] which, as shown previously, are key intermediates in various carbonylation reactions catalysed by palladium complexes. The direct palladisation of aromatic compounds thus opens a pathway to their use as the initial substrate in the synthesis of carbonyl-containing products. The possibility of the practical realisation of this idea has been demonstrated in a number of studies.[36,133-140] It has been shown[133] that substituted benzenes as well as thiophen and furan react with palladium acetate and CO at 15 atm and 100 °C to form the corresponding carboxylic acids [the yields of the mixture of regio-isomers are given relative to $Pd(OAc)_2$]:

$$ArH + Pd(OAc)_2 \xrightarrow{CO} \underset{14\text{–}48\%}{ArCO_2H} + Pd .$$

ArH = C_6H_6, PhOMe, PhMe, PhCl, thiophen, furan

The sequence of the reactivities of the aromatic compounds (PhOMe > PhMe > C_6H_6 > PhCl) and the preferential *ortho-*, *para*-directing effect in the carboxylation reaction in the presence of *ortho*, *para*-directing substituents in the initial benzene (MeO, Me, Cl) indicates the electrophilic character of the process. The proposed mechanism of the carboxylation of arenes[133] is shown schematically below:

$$ArH + Pd(OAc)_2 \rightarrow ArPdOAc + HOAc ,$$

$$ArPdOAc + CO \rightarrow ArCOPdOAc ,$$

$$ArCOPdOAc \rightarrow ArCOOAc + Pd ,$$

$$ArCOOAc + HOAc \rightarrow ArCO_2H + Ac_2O .$$

It is of interest that, in the presence of certain organic halides, for example, 1,2-dibromoethane, the interaction of ArH with CO and $Pd(OAc)_2$ does not lead to carboxylic acids but affords their anhydrides $(ArCO)_2O$.[134]

According to the scheme presented above, in order to make the reaction catalytic it is essential to add an oxidant capable of converting the inactive zerovalent palladium into a palladium(II) salt. It has been suggested that $FeCl_3$,[135] $Tl(O_2CCF_3)_3$ (in this case the substrate may be an organothallium compound formed *in situ* and not the arene itself—see Section II),[36] $CuCl_2$,[136] $Na_2S_2O_8$,[137,138] and t-BuOOH[139] be used as the oxidants. However, the yield of the carbonylation product and the selectivity of the catalytic process are usually low, for example:[135,139]

$$C_6H_6 \xrightarrow[75\ ^\circ C\ t\text{-}BuOOH]{Pd(OAc)_2,\ 1\ atm\ CO} \underset{1300\%}{PhCO_2H} + \underset{1500\%}{Ph_2} + \underset{200\%}{PhOH} ,$$

$$MePh \xrightarrow[125\rightarrow 175^\circ C,\ FeCl_3]{PdCl_2,\ 48\ atm\ CO} \underset{520\%}{4\text{-}MeC_6H_4CO_2H} .$$

The yields are quoted relative to the palladium(II) salt.

The reaction of substituted arenes frequently yields mixtures of regioisomeric acids which are difficult to separate (1 atm CO, 75 °C):[139]

$$PhOMe \xrightarrow[t\text{-}BuOOH]{Pd(OAc)_2,\ CO} MeOC_6H_4CO_2H .$$

The yields, calculated relative to $Pd(OAc)_2$, of the *ortho*-, *meta*-, and *para*-products are 126, 8, and 123% respectively.

The interaction of substituted benzenes with palladium acetates in a CO_2 atmosphere also leads to aromatic acids.[140] In the presence of t-BuOOH, the reaction becomes weakly catalytic with respect to palladium (1 atm CO_2, 70 °C):

$$RPh \xrightarrow[t\text{-}BuOH]{Pd(OAc)_2,\ CO_2} RC_6H_4CO_2H\ .$$

R=Me (125%), H (127%), Cl (40%)

[the yields are quoted relative to $Pd(OAc)_2$]

Thus the carbonylation of arenes, which is of considerable interest because of the ready availability of the initial reactants, encounters major difficulties. The main problem is the low yield of the products and the low selectivity of the reaction.

Apart from arenes, the hydrogen atom can be replaced by CO only in the 1-position in terminal acetylenes (1 atm CO, 20 °C):[141]

$$RC{\equiv}CH + R'OH \xrightarrow[CuCl_2,\ NaOAc]{cat.\ Pd,\ CO} \underset{58-74\%}{RC{\equiv}CCO_2R'}\ .$$

R = n-C_5H_{11}, Ph, $PhOCH_2$; R'=Me, iso-Pr

The reaction is catalysed by 6 mole% of $PdCl_2$ using copper dichloride or *p*-benzoquinone as the oxidants.

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The Kinetic Stability of Biscyclopentadienyl and Diarene Compounds of Transition Metals in the Thermal Decomposition Reaction

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Literature data on the kinetic stability of mononuclear metallocene and diarene derivatives of transition metals are described systematically and discussed. A relation between the reactivity of the π-complexes in the thermal decomposition reaction and their structure (the nature of the central metal atom, the σ-substituent, and the π-ligand) has been discovered, surface effects and the role of the adsorption of organometallic compounds in pyrolysis are examined, and problems of macrokinetics are discussed.
The bibliography includes 106 references.

CONTENTS

I. Introduction 316
II. Kinetics of the thermal decomposition of the π-complexes of transition metals 316
III. Surface reactions in the pyrolysis of organometallic compounds 318
IV. Macrokinetics of the thermal decomposition 320
V. The mechanism of pyrolysis 320

I. INTRODUCTION

The study of the thermal stability of organometallic compounds (OMC) is of great theoretical and practical interest. The kinetic stability of mononuclear metallocene and diarene derivatives of metals is, together with their volatility, the fundamental characteristic determining the possibility of their practical use for the preparation of solid fuels,[1] various coatings,[2,3] and catalysts of many chemical processes.[4,5] Furthermore, a systematic analysis of the relevant literature data has not so far been carried out; in the present review, such an attempt is made for the first time.

Four aspects of the stability of OMC in synthesis–decomposition processes have been distinguished.[2,3] They embrace the molecular and electronic structure of organometallic compounds, their state of aggregation, their dynamics, and their interaction with energy and mass fluxes: the stability of an isolated molecule and of the decomposition products (quantum-chemical aspect), the stability of the sum of the molecules in equilibrium with their decomposition products (thermodynamic aspect), the rate of change in the equilibrium of the sum of the molecules (the kinetic aspect), and the phenomenon of mass and heat transfer in assemblies of molecules (macrokinetic aspect).

The quantum-chemical aspects of the stability of the molecules of certain π-complexes of metals[2,3,6-9] as well as the thermodynamic stability of metallocene and diarene derivatives of metals[2,3,10-17] have been described in the literature. An account has been given of the ideas concerning the stability of OMC in the synthesis–decomposition processes.[18]

The present review describes systematically, and surveys, experimental data on the kinetic and macrokinetic stability of mononuclear metallocene and diarene derivatives of transition metals in the thermal decomposition reaction. Questions concerning the reactivity of the OMC and its relation with the structure (the nature of the metal and ligand), the mechanism of the decomposition process, surface effects, adsorption, and the spatial localisation of the reaction are examined. In connection with the macrokinetic studies, the thermal decomposition reaction is considered taking into acount the heat and mass exchange. The kinetic parameters of the thermal decomposition of the OMC referring to the overall process are analysed and described systematically. These data have been analysed under comparable conditions. The review does not include any data on the deposition of metallic, oxide, and composite coatings obtained by the pyrolysis of OMC by the gas-thermal method, which have already been described systematically in the specialist literature[19,20] and in reviews[21,22] and also data on the photochemical decomposition of metallocenes.[23]

II. KINETICS OF THE THERMAL DECOMPOSITION OF THE π-COMPLEXES OF TRANSITION METALS

1. The Role of the Nature of the Central Metal Atom

The systematic study of the kinetics of the gas-phase decomposition of metallocenes began two decades ago with the investigation of the thermal stability of ferrocene and its substituted derivatives.[24,25] The kinetic study of the thermal decomposition of π-complexes has been carried out under static conditions by the manometric method and under dynamic conditions by a gas-chromatographic pulse method.[26] The apparent rate constants for the overall reaction, calculated for low degrees of decomposition where the influence of the products formed can be neglected, were used as a measure of the reactivity. The kinetic parameters were compared under comparable conditions in the temperature range where the kinetic regime operates.

The pyrolysis of ferrocene,[25] ruthenocene, and osmocene[27] is strikingly autocatalytic, the metal-containing solid phase serving as the catalyst. It has been established that, in vessels treated with pyrolytic iron, the kinetic stability of metallocenes of the iron subgroup increases with increase in the average dissociation energy of the ring–metal bond in the sequence ferrocene < ruthenocene < osmocene.[28]

In contrast to the iron-subgroup metallocenes, the pyrolysis of vanadocene,[29] chromocene,[30] manganocene,[30] cobaltocene,[31] and nickelocene[32] is described satisfactorily by first-order kinetic equations.

The nature of the central metal atom determines the kinetic stability of the mononuclear metallocenes[33,34] (Table 1).

Among metallocenes of the series of 3*d* metals, ferrocene, being an 18-electron complex,[2] exhibits the highest kinetic stability. The π-complexes of metals located to the left and to the right of iron in the Periodic Table are characterised respectively by a deficiency or

an excess of electrons at the central metal atom compared with ferrocene[7-9] and are less stable (Table 2).

Table 1. Kinetic parameters of the pyrolysis of the metallocenes Cp_2M (Cp = cyclopentadienyl) under static conditions*.[33,34]

t, °C	Cp_2V		Cp_2Cr		Cp_2Mn		Cp_2Co		Cp_2Ni	
	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}
550	51	1.03	60	3.80	—	—	—	—	—	—
540	81	0.69	—	—	—	—	—	—	—	—
520	38—180	0.31	45—78	2.10	—	—	—	—	—	—
500	59	0.14	36—196	1.34	175	7.20	117	3.30	—	—
480	—	—	105	0.85	261	4.40	130	2.15	—	—
470	—	—	—	—	—	—	71	1.70	—	—
460	—	—	94	0.48	139	2.50	—	—	—	—
450	—	—	—	—	—	—	45—280	1.17	—	—
440	—	—	—	—	92	1.30	—	—	—	—
420	—	—	—	—	103	0.84	—	—	151	5.78
380	—	—	—	—	—	—	—	—	150	2.36
360	—	—	—	—	—	—	—	—	120—200	1.55
350	—	—	—	—	—	—	—	—	149	1.00
340	—	—	—	—	—	—	—	—	151	0.76

*The activation energy (E, kcal mol^{-1}) and the pre-exponential factor [lg $A(s^{-1})$] are respectively 50.5 ±0.66 and 10.41 ±0.18 for Cp_2V, 27.3 ± 0.8 and 4.87 ± 0.23 for Cp_2Cr, 29.3 ± 1.2 and 6.61 ± 0.35 for Cp_2Mn, 23.1 ± 1.0 and 4.04 ± 0.31 for Cp_2Co, and 21.4 ± 0.2 and 4.52 ± 0.37 for Cp_2Ni.

Table 2. Thermodynamic parameters and comparative kinetic stabilities of metallocenes in their decomposition in a glass reactor under static conditions (at 500 °C).[16,17,33]

Compound	$\bar{D}$(M-Cp), kcal mol^{-1}	ΔS(M-Cp), cal mol^{-1} K^{-1}	ΔG(M-Cp), kcal mol^{-1}	r (M—C), Å	$10^3 k$, s^{-1}
Cp_2V	88	47	74	2.280	0.14
Cp_2Cr	67	40	55	2.169	1.34
Cp_2Mn	51	35	40	2.383	7.20
Cp_2Fe	72	41	60	2.064	0.01
Cp_2Co	64	41	52	2.119	3.30
Cp_2Ni	60	37	49	2.196	29.50
Cp_2Fe *	72	41	60	2.064	11.8
Cp_2Ru *	99	—	—	2.208	1.90
Cp_2Os *	109	—	—	2.220	0.77

*The walls of the glass reactor were coated by the solid products of the pyrolysis of ferrocene.

For the electron-deficient complexes of 3*d* metals (vanadocene > chromocene > manganocene), the thermodynamic characteristics of the dissociation of the ring—metal atom bond (the average Gibbs free energy $\Delta\bar{G}$ and the average dissociation energy $\bar{D}$) and the kinetic stability vary in parallel. The contribution of the entropy change $\Delta\bar{S}$ to $\Delta\bar{G}$ is insignificant.[16] For the complexes of the metals in the iron triad, the decrease in thermal stability in the sequence ferrocene > cobaltocene > nickelocene is correlated with the decrease in the average dissociation energy in the above bond and with the population of the antibonding orbitals of the metallocene. In ferrocene, these orbitals are unoccupied, in cobaltocene they contain one electron, and in nickelocene they contain two electrons.[7]

Thus a monotonic variation of the kinetic stability of the metallocenes in the 3*d* series has not been observed:

$$Cp_2V > Cp_2Cr > Cp_2Mn \ll Cp_2Fe \gg Cp_2Co > Cp_2Ni.$$

In the Group VIII of the Periodic System, the kinetic stability of the metallocenes of the iron subgroup increases with increase in the atomic number of the metal.

The kinetic stability of the metallocene is not correlated with characteristics of the electronic structure such as the negative charge on the metal atom, the M—C bond indices,[9] and the number of unpaired electrons[8] and also no correlation is observed with the molecular structure (the M—C bond length[8]) and with the so called "decomposition temperature" which has no definite physical significance.[28,35]

The thermal stability of the diarene complexes of chromium, molybdenum, and vanadium increases with increase in the average dissociation energy of the six-membered ring—metal atom bond[36-38] (Table 3).

Table 3. Kinetic parameters of the gas-phase pyrolysis of diarene complexes of chromium, molybdenum, and vanadium.[36—38]

Compound	t, °C	E, kcal mol^{-1}	lg A (s^{-1})	$10^3 k$, s^{-1} (380 °C)
Dibenzenechromium	340—400	23.5±0.5	—	1.55
Di(ethylbenzene)chromium	320—400	25.0±1.0	5.7±0.4	2.26
(Ethylbenzene)(diethylbenzene)chromium	320—380	41.0±0.5	11.2±0.23	2.95
Di(ethylbenzene)molybdenum	340—400	42.1±0.6	10.9±0.2	0.69
Di(diethylbenzene)molybdenum	340—380	31.9±2.1	7.7±0.7	0.90
(Ethylbenzene)(diethylbenzene)molybdenum	340—400	36.9±1.4	9.4±0.5	0.93
Di(ethylbenzene)vanadium	360—480	22.3±0.5	3.8±0.4	0.22

The kinetic stability of the diarene derivatives of metals corresponds to the average dissociation energy, found by the thermochemical method, of the bond between the metal atom and the six-membered ring, which diminishes along the first series of transition elements and increases along the Group with increase in the atomic number of the transition metal.[12,13]

2. The Influence of the Substituent in Cyclic π-Ligands

The nature of the substituents in aromatic rings influences the kinetic stability of metallocene[25,35,39,40] and diarene derivatives of metals[37,38,41] (Tables 3 and 4). The activity of ferrocenes is attributed to the polar influence of the substituents and also to the stability of the radical formed on homolysis of the cyclopentadienyl ring—substituent bond. The influence of electron-donating alkyl substituents on the reactivity of the ferrocene nucleus is inductive in character, like the transfer of this influence via the iron atom to the other ring.[25] Little is known about the character of the influence of electron-accepting substituents on the thermal stability.

Under both static and dynamic conditions, the thermal stability of ferrocene increases with increase in the thermodynamic stability of the groups formed when the side chain is split off homolytically. The accumulation of t-butyl groups in the ferrocene nucleus increases the thermal decomposition rate constant to a much greater extent than the replacement of one alkyl group by another. This effect is especially pronounced on passing from heteroannular tri-t-butyl- and tetra-t-butyl-ferrocenes, in which the t-butyl groups are in different cyclopentadienyl rings of the ferrocene nucleus. Thus substitution of two hydrogen atoms by t-butyl groups in one cyclopentadiene ring of ferrocene increases the rate constant by a factor of 15, while the introduction of a further two t-butyl groups in the other ring increases the rate constant by a factor of 300. A similar relation can be traced also for ferrocenes with electron-accepting substituents. Evidently steric effects also play a decisive role in the kinetic stability of polysubstituted ferrocenes.

Analysis of data obtained shows that both electron-donating (alkyls) and electron-accepting (acetyl) substituents accelerate the decomposition of ferrocene. Here the introduction of one electron-accepting group lowers the thermal stability of ferrocene to a much greater extent than the introduction of any electron-donating group. Heteroannular polysubstituted ferrocenes with electron-accepting substituents are thermally the most stable. The introduction of an alkyl substituent into the cyclopentadienyl ring of nickelocene influences the reactivity to a lesser extent than in the case of ferrocene, the rate constant for the thermal decomposition of substituted nickelocene increasing by less than a factor of two.

The kinetic stability of the bisarene derivatives of chromium and molybdenum investigated hardly changes in the thermal decomposition reaction on passing from the diethyl to the triethyl and tetraethyl derivatives. This agrees well with the conclusion[13] that the influence of the alkyl substituent in the benzene ring of bisarene derivatives of metals on the average dissociation energy of the metal atom–ring bond is within the limits of experimental error.

Table 4. The influence of the substitutent on the rate of pyrolysis of metallocenes in closed and open systems.[34,36-38]

Compound	t, °C	$10^3 k$, s^{-1}	V^*_{rel}
Closed system			
Ferrocene	550	0.01	1
Ethylferrocene	550	0.05	5
Butylferrocene	560	0.11	—
"	550	0.07	7
Di-t-butylferrocene	560	0.16	—
"	550	0.15	15
1,1',3-Tri-t-butylferrocene	550	2.00	200
"	510	0.34	—
"	450	0.03	—
1,1',3,3'-Tetra-t-butylferrocene	550	3.02	300
"	500	0.32	—
"	480	0.12	—
Acetylferrocene	560	1.40	—
"	550	1.00	100
"	530	0.52	—
1,1'-Diacetylferrocene	550	4.47	447
"	520	1.50	—
"	500	0.67	—
Nickelocene	380	2.36	—
"	360	1.60	—
Diisopropylnickelocene	380	3.50	—
"	360	2.11	—
Open system			
Ethylferrocene	500	66	—
"	450	9	1
Diethylferrocene	500	79	—
"	450	18	2
t-Butylferrocene	500	97	—
"	450	36	4

* V_{rel} is the ratio of the [pyrolysis?] rate constant to the rate constant for the decomposition of ferrocene at 550 °C.

3. The Influence of the Nature of the Cyclic π-Ligand

The reactivity of π-complexes of chromium is determined by the character of the ring linked to the metal atom. A comparative study has been made[42] of the kinetics of the thermal decomposition of the π-complexes of chromium with six-membered and five-membered cyclic π-ligands. It was shown that dibenzenechromium is less stable than chromocene. Thus dibenzenechromium and chromocene decompose at almost equal rates at 360° and 460 °C respectively (the rate constants are 0.35×10^{-3} and 0.48×10^{-3} s^{-1} respectively). It is known[16] that not only the average dissociation energy but also other thermodynamic characteristics of the metal–ligand bond dissociation ($\Delta\bar{G}$ and $\Delta\bar{S}$) diminish on passing from $(C_5H_5)_2Cr$ to $(C_6H_6)_2Cr$, the contribution of $\Delta\bar{S}$ to $\Delta\bar{G}$ being insignificant. Furthermore, these compounds decompose via different pathways: the radical pathway for $(C_2H_5)_2Cr$ and the molecular pathway for $(C_6H_6)_2Cr$. The latter pathway leads to the formation of chromium in an active state and to the autocatalytic acceleration of the decomposition of dibenzenechromium.

III. SURFACE REACTIONS IN THE PYROLYSIS OF ORGANOMETALLIC COMPOUNDS

1. The Spatial Localisation of the Reaction

Features characteristic of a homogeneous-heterogeneous process have been observed in the study of the pyrolysis of metallocenes[43] and bisarene derivatives of metals.[44] The rate of thermal decomposition of metallocenes of the iron triad (especially ferrocene and its alkyl derivatives) depends greatly on non-controllable changes in the state of the walls of the glass reaction vessel.

The metal-containing products of the pyrolysis of metallocenes exhibit an autocatalytic activity. The autocatalytic character of the decomposition of the iron subgroup metallocenes was noted above.[32,35] The rate constant for the pyrolysis of ferrocene on its own decomposition products is higher by three orders of magnitude than in clean glass vessels.[25]

The catalytic activity of the metal-containing solid phase segregated in the pyrolysis of metallocenes depends on the nature of the central metal atom. Pyrolytic osmium accelerates the thermal decomposition of osmocene to a greater extent than pyrolytic ruthenium accelerates the decomposition of ruthenocene, while pyrolytic iron is more active in the decomposition reaction of ferrocene than is osmium in the decomposition of osmocene. The catalytic activity of the pyrolytic metals in relation to the decomposition of ferrocene falls in the sequence osmium > iron > ruthenium.[27]

The solid products of the pyrolysis of vanadocene, chromocene, manganocene, cobaltocene, and nickelocene are less active and their catalytic effect is small and disappears during the experiment as a result of adsorption of cyclopentadiene on the active centres produced in the reaction. The absence of the autocatalytic acceleration in the thermal decomposition of the cyclopentadienyl derivatives of vanadium, chromium, manganese, cobalt, and nickel in clean glass vessels can be accounted for precisely by the decrease in the catalytic activity of the surface during the experiment.[34]

It has been shown[43] that, under static conditions, the heterogeneous decomposition of metallocenes on solid metal-containing products does not occur and the role of the heterogeneous processes reduces to initiating the gas-phase reaction, developing subsequently within the volume of the reactor. An analogous investigation of the surface effect in the pyrolysis of bisarene derivatives of metals[44] has demonstrated an appreciable dependence of the rate of reaction on both the nature and the area of the surface.

Coatings obtained by the pyrolysis of ditoluenechromium iodide, ferrocene, and carbonylruthenium chloride are the most active, accelerating the decomposition of the bisarene derivatives of chromium, molybdenum, vanadium by a factor of 30–50. The solid products of the pyrolysis of the diarene derivatives themselves and the nickel–carbon coating obtained by the decomposition of diisopropylnickelocene are less active coatings, accelerating the decomposition by a factor of only 3–5.

The rate of decomposition of the diarene derivatives of metals, except dibenzenechromium, depends to a large extent on the surface

area of the reaction vessel (Table 5). The effective rate constant for the decomposition of (ethylbenzene) (diethylbenzene)-chromium increases linearly with increase in the ratio of the surface area of the reactor to its volume.[37,44,45] The contribution of the homogeneous component to the overall process increases with increase in temperature and with decrease in the surface to volume ratio, while the contribution of the heterogeneous component actually falls under these conditions. The purely heterogeneous course of the process and a decrease in the kinetic stability of the diarene derivatives of metals have been observed when the thermal decomposition was carried out in a high vacuum.[45]

Table 5. The influence of the surface area on the rate constants for the pyrolysis of diarene complexes of metals in glass vessels.[37,44,45]

Compound	t, °C	S/v, cm^{-1}	$10^3 k$, s^{-1}
Dibenzenechromium	380	1.5	1.55
	380	18.0	1.55
	380	18.0*	1.55
Di(ethylbenzene)chromium	360	1.8	1.06
	360	2.5	2.65
	380	1.8	2.26
	380	2.5	4.40
(Ethylbenzene)(diethylbenzene)chromium	320	1.8	0.12
	320	2.5	0.32
	320	6.8	1.53
	320	8.5	2.61
	320	11.5	3.50
	320	25.0	8.20
Di(ethylbenzene)molybdenum (mixture of isomers and homologues)	340	1.5	0.10
	340	12.8	3.30
	380	1.5	0.69
	380	12.8	5.10
(Ethylbenzene)(diethylbenzene)molybdenum	340	1.8	0.16
	340	8.0	7.10
	380	1.8	0.98
	380	8.0	7.10
Di(ethylbenzene)molybdenum	360	1.8	0.50
	360	7.2	1.50
	360	9.0	6.70
Di(ethylbenzene)vanadium (mixture of isomers and homologues)	450	1.5	1.10
	450	12.8	1.22

* "Packing" coated with pyrolytic chromium.

The kinetics of the heterogeneous thermal decomposition reaction of the diarenechromium π-complexes have been investigated in a stream of carrier gas[46,47] and also in closed and circulation systems.[48] In the kinetic region (305–350 °C), the order of the reaction changes from first to zero with increase in the OMC concentration, while in the diffusion region (360–600 °C) the reaction is first order. From the kinetic data presented,[48] one may conclude that the reactivity of the diarenechromium complexes changes little on passing from dibenzenechromium to its ethyl derivatives.

Thus the localisation of the reaction in space is determined by the experimental conditions on which depends the purely homogeneous, heterogeneous, or homogeneous-heterogeneous course of the process. Such conditions include the initial pressure and the concentration of the initial diarene derivatives of the metal,[45,48,49] the heterogeneous factor S/V (the ratio of the internal surface area of the reactor to its volume),[44,45] and the nature of the surface and the methods used to produce it.[44]

For the thermal decomposition of the diarene derivatives of chromium, molybdenum, and vanadium at the metal–ligand bond in a reactor of limited size with walls exhibiting a catalytic activity, a kinetic model has been proposed in which it is suggested that the reaction proceeds via a unimolecular mechanism complicated by phenomena involving the association of the OMC molecules or the formation of their complexes with the molecules of catalytic additives.[51] This model makes it possible to explain the experimentally observed dependence of the effective rate constant for the process on the initial pressure, the S/V ratio, the chemical activity of the surface of the reactor, and the degree of complex formation with the molecules of the catalytic additives.[52]

2. Adsorption Effects in Thermolysis

The high adsorption capacity of the OMC is widely known.[3,53] The adsorption of organometallic compounds and their decomposition products is one of the stages of the heterogeneous process influencing the rate and mechanism of the decomposition.

Two forms of adsorption have been observed by direct IR spectroscopic studies of the adsorption complexes of OMC[54-56] on surfaces modified by pyrolytic chromium: physical adsorption resulting from the ligand–surface interaction, chemical adsorption which is a consequence of the formation of a metal–surface or CO–surface (for OMC with carbonyl ligands) bond. On chemisorption, ferrocene forms charge-transfer complexes in the form of ferricenium[53,56] and ferrocenonium[56] cations.

A mechanism has been proposed for the catalytic decomposition of 1,1'-diethylferrocene on alumina involving its adsorption on the active surface centres with formation of the alkylferrocenium cation and its subsequent decomposition in the adsorbed state with segregation of an iron-containing solid phase having a polymeric structure.[57] The formation of σ- and π-complexes of cyclopentadiene following its adsorption on Group VIII metals has been observed spectroscopically.[58] The strong specific interaction of the surface chromium atoms, obtained by the decomposition of diarenechromium, with the six-membered rings of the substituted benzenes involving the formation of π-complexes has been demonstrated by gas chromatography.[59]

The influence of the adsorption of the OMC and of their decomposition products in the absence and presence of various additives on the rate of deposition and the properties of the resulting coating have been described in a number of studies.[60-64] The character of the intermolecular interaction of alkylferrocenes and (ethylbenzene) (diethylbenzene)chromium with the metallated and non-metallated surfaces under conditions approaching those in the thermal decomposition has been studied.[65] At temperatures above 200 °C on surfaces metallated by pyrolytic chromium, the contribution of the specific interaction of the diarenechromium molecules with the surface, leading to chemisorption, increases. Thus the isosteric heat of adsorption of (ethylbenzene) (diethylbenzene)-chromium on pyrolytic chromium at low degrees of coverages reaches 46 kcal mol^{-1}, while after the attainment of 20% coverage it falls to the limiting value of 27.5 kcal mol^{-1}. On the other hand, after its adsorption on quartz only non-specific adsorbate—adsorbent interactions (the isosteric heat of adsorption at 10% coverage is 1 kcal mol^{-1}) or weak interactions of the adsorbed diarenechromium molecules with one another (the isosteric heat of adsorption at a coverage above 10% is 5 kcal mol^{-1}) were observed. The following series based on the adsorption capacity of the compounds has been obtained from the heats of adsorption: (ethylbenzene) (diethylbenzene)chromium > ethylferrocene > ethylbenzene > benzene.[65]

Comparison of the adsorption capacities of ethyl- and butylferrocenes on quartz, pyrolytic iron, and chromium showed that the isosteric heats of adsorption at high coverages (starting from 20%) are similar (13.0 ± 0.5 kcal mol^{-1}), which is characteristic of physical adsorption.[65] Only at low coverages (5–10%) are strong specific interactions manifested between ethylferrocene (19.5 kcal mol^{-1}) and the most active centres on the surface metallated by pyrolytic iron, probably occurring with formation of charge-transfer adsorption complexes.

IV. MACROKINETICS OF THE THERMAL DECOMPOSITION

The study of the macrokinetics of the thermal decomposition of OMC has been undertaken in view of the practical interest in such compounds as sources of metallic and composite coatings.

In the decomposition of diarenechromium on a support in an open system at a constant rate of evacuation, the phenomenon of "peak" (maximum) rate of deposition of the coating, due to the change in the partial pressure of the OMC near the support owing to the increase in the concentration (pressure) of the volatile products liberted, has been observed.[3,6] The causes of the decrease in the rate of deposition are also the endothermicity of the thermal decomposition process and the decrease in the temperature of the support.[66-69]

There exist two types of conditions for the deposition of coatings from the vapour phase in the thermal decomposition of OMC[3,6,69-71]—monotonic and vibrational (including the conditions in a closed system)—which have been revealed by the changes in the pressure, the temperature of the support, and the rate of deposition of the coating. The vibrational phenomena and the causes of their appearance have been examined in detail.[3] The vibrational conditions lead to the appearance of a layered structure of the film with alternation of layers of the metal or metal carbide with different contents of carbon-containing products.

The kinetics of the growth of the layer of pyrolytic chromium in the decomposition of diarenechromium derivatives in a stream of an inert gas have been investigated[41] taking into account heat and mass exchange. The rate of growth was calculated with the aid of the model proposed by Patankar and Spalding[72] and Popov and Rabinovich[73] using the rate constants for the decomposition of the diarene derivatives of chromium in a stream of helium.[41] With increase in temperature in the deposition zone from 350° to 500 °C, the rate of growth of the chromium layer also increases, but the non-uniformity of the distribution along the length of the channel diminishes (the deviation from the uniform distribution increases from 2.6% to 36% respectively). With increase in the concentration of the diarene derivatives of chromium, the rate of growth also increases and the uniformity of the growing layer is improved. On the other hand, an increase in the flow rate of the gas mixture diminishes the rate of growth of chromium but the uniformity of its distribution along the length of the channel also improves. In order to attain high rates of growth of the coating, it is necessary to raise the concentration of the OMC introduced at a temperature in the deposition zone in the range 350°–400 °C and for the optimum flow rate of the gas mixture.

The influence of various factors (channel temperature, flow rate of gas mixture, concentration of the initial substance) on the distribution of the solid products of the pyrolysis of ethylferrocene along the length of the channel has been investigated analogously and the rates of growth of the layer of the iron-cross-linked polymer on the surface have been determined.[40] With increase in the pyrolysis temperature from 400° to 550 °C, an increase in the rate of growth and a decrease in the uniformity of the growing layer along the length of the channel are observed. An increase in the concentration of the ethylferrocene introduced leads to an increase in the rate of growth virtually without change in the uniformity of the growing layer along the deposition zone. An increase in flow rate of the gas mixture tends to decrease the rate of growth of the layer but improves significantly its uniformity (at flow rates of 1 and 3 litre min^{-2}, the deviation from uniformity at 400 °C is 8.4 and 0.1% respectively). The highest rate of growth of the coating combined with the best uniformity of the distribution is attained at 500 °C and for a flow rate of the gas mixture of 2 litre min^{-1}. These conclusions apply only to the given specific dimensions of the reactor, gas flow conditions, and the composition of the gas mixture.

V. THE MECHANISM OF PYROLYSIS

1. Thermal Decomposition Products and Pathways

The thermal decomposition of the π-complexes of transition metals is accompanied by the homopolar dissociation of the metal–ligand bond with formation of the metal and radicals or the metal and ligand molecules.[2,3] OMC whose ligands have an odd number of bonding electrons decompose via the radical pathway, while those having an even number of such electrons decompose via the molecular pathway.[64] The pyrolysis is usually a multistage process, the ease of the occurrence of which and the pathway followed are determined by the nature of the OMC, the metal–ligand bond dissociation energy, the ratios of this energy to the C–C and C–H bond dissociation energies in the ligand, the polarity of the metal–ligand bond,[2,3,6] and also the degree of shielding of the central metal atom by the ligands, i.e. by steric effects.[74]

A free radical mechanism, involving the homolytic cleavage of the metal–ligand bonds and the C–C and C–H bonds in the ligand, is usually proposed for the decomposition of the mononuclear cyclopentadienyl compounds of transition metals.

The main product of the non-extensive gas-phase pyrolysis of ferrocene is hydrogen, methane and carbon monoxide are formed from acetylferrocene, and ethane is formed from ethylferrocene. This agrees with the hypothesis that a hydrogen atom is initially abstracted from the ferrocene nucleus in the unsubstituted ferrocene and that the side chain (CH_3CO and C_2H_5) is split off from the cyclopentadienyl ring in the substituted ferrocenes.[25] The dependence of the yield of the main pyrolysis products of ferrocenes on the nature of the surface and on its area and also on the added inhibitors shows that the heterogeneous stages of the free-radical mechanism of the decomposition reaction are both the generation and destruction of the radicals.

The thermal decomposition of ferrocene in the condensed phase at relatively low temperatures is accompanied by the dissociation of the C–H bonds with formation of the pyrolysis product—biferrocenyl.[75] The same mechanism of the decomposition reaction—not at the metal—ligand bond but at the C–C and C–H bonds—has been proposed also for the decomposition of alkylferrocenes by electron impact.[76] At high temperatures, in the pyrolysis of ferrocene above 800 °C, the cleavage of the ring–metal atom bond is observed with formation of the cyclopentadienyl radical, which has been detected spectroscopically.[77] Indeed, cyclopentadiene has been found together with methane and ethylene in the products of the pyrolysis of ferrocene above 600 °C.[28]

The pyrolysis products of ruthenocene and osmocene have not been investigated. Only the existence of the dimeric forms of ruthenocene and osmocene in the gas phase has been established.[78] The main gaseous products of the pyrolysis of other metallocenes for low degrees of decomposition are cyclopentadiene, hydrogen, and methane.[33] The composition of the volatile products depends on the temperature and the degree of decomposition.

Apart from cyclopentadiene, naphthalene, and nickel, 9,10-dihydrofulvalene, which is the product of the recombination of the cyclopentadienyl radicals, has been found among the products of the pyrolysis of nickelocene[79] *in vacuo* under pulse conditions at 950 °C. The cyclopentadienyl dimer has also been detected[28] in the decomposition of cyclopentadienylcarbonylman- ganese. The main products of the decomposition of nickelocene in a stream of hydrogen[80] were cyclopentadiene, cyclopentene, and cyclopentane. The purity of the nickel segregated was 83–93%.

It has been suggested that the pyrolysis of metallocenes involves the abstraction of hydrogen from the cyclopentadienyl ring and the subsequent polyrecombination of the metal-containing radical. The metal-containing radicals formed are also capable of being dehydrogenated and of undergoing subsequent condensation, affording ultimately carbide-like structures.[2,32]

Apart from the metal-containing phases, substances have been detected in the pyrolysis products which appear as a result of the condensation of five-membered rings (ranging from the cyclopentadiene dimer to the pentamer) and also naphthalene, anthracene, phenanthrene, pyrene, and perylene.[32] Volatile products containing metal–carbon phases, tentatively assumed to be polymeric in nature, are also formed.[25,57]

The main reactions leading to the decomposition of unsubstituted metallocenes involve the cleavage of the ring–metal atom bond and the dehydrogenation of the metallocene, the contribution of the dehydrogenation reaction increasing in the sequences Cp_2Ni < Cp_2Co < Cp_2Fe and Cp_2Mn < Cp_2Cr < Cp_2V. The decrease in the contribution by the dehydrogenation reaction takes place in parallel with the decrease in the kinetic stability of the 3*d* metal metallocenes.[33]

The mechanism of the decomposition of the diarene derivatives of transition metals on heating[2,64,81-91] in a strong electric field,[92] in a high-frequency discharge,[93] and under the influence of electron impact[94] has been discussed widely in the literature. It is suggested that the process takes place almost quantitatively via a molecular mechanism involving the abstraction of ligands and the segregation of the metal.[2,3,64]

Gaseous compounds (hydrogen, methane, and C_2–C_5 paraffinic and olefinic hydrocarbons), liquid compounds (benzene, and ethyl-, diethyl-, and triethyl-benzenes), and solid compounds (biphenyl, terphenyl, ethyldiphenylcyclohexanes, carbon, metal carbides, and the metal) have been found in the products of the thermal decomposition of the diarene derivatives of vanadium, chromium, and molybdenum under static conditions. The main process involving the decomposition of the metal–ligand bond is accompanied by secondary ligand decomposition reactions[95,96] via catalytic dehydrogenation stages[87,88,95] and the subsequent formation of carbon-containing condensed products. It also proceeds via the elimination of methylene from the ligand side groups (for example, ethylbenzene), whose subsequent reaction leads to the formation of methane, carbon, and hydrogen.

In a flow system,[87,88,97] the primary ligand conversion reaction is also their dehydrogenation accompanied by the formation of aryl radicals whose recombination leads to the formation of biphenyls and other condensed substances which are dehydrogenated to carbon in the presence of the metal. Graphite has been detected in the condensation products by electron diffraction.[66] The amount of gaseous products in an open system is smaller by an order of magnitude than in a static system, the only gaseous product being hydrogen.

Thermographic and gas-chromatographic studies have shown[81] that the thermal decomposition of dibenzenechromium at the metal-ligand bond at reduced pressures takes place stepwise with the consecutive elimination of ligands, the energy of the abstraction of the first ligand being greater than that of the second.

Together with the preferential molecular decomposition of diarene derivatives of metals at the metal–ligand bond, radical decomposition takes place to some extent, proceeding via the $\pi-\sigma$ rearrangement of the initial compound[97,98] with formation of a hydrogen atom and aryl radicals. The formation of aryl radicals from the diarene derivatives of chromium, vanadium, and molybdenum has been demonstrated by their fixation on anthracene and ferrocene. A radical chain mechanism of the pyrolysis of di(ethylbenzene)chromium has also been proposed by Dudorov et al.[99]

2. Elementary Steps in the Thermal Decomposition Reaction

The common features of the radical and molecular mechanisms of the thermal decomposition of OMC proceeding with retention of the orbital symmetry (the Woodward–Hoffmann rule) and of the total spin of the system (the Wigner–Witmer rule) have been examined in detail by Razuvaev and co-workers.[2,3] A common feature of the radical and molecular decomposition pathways from the standpoint of the conservation rules, is that the most favourable activated state of the OMC molecule is the OMC triplet dissociating via the metal–ligand bond with formation of either a pair of radicals in the triplet state or ligand molecules and the metal in the excited triplet state.

A quantum-chemical description of the elementary step in the thermal decomposition at the metal–ligand bond has been achieved for diarenechromium[3,6,100] within the framework of the method of one-electron molecular orbitals. The dissociation of the metal–ligand bond can occur in an OMC molecule in an excited electronic state, arising when a light quantum is absorbed or as a result of the interaction with the medium. For dibenzenechromium, the energetically most favourable course of this reaction is via the triplet state of the OMC molecule with formation of the arene in the triplet state and of a chromium atom in a state other than the ground state. The possible pathways leading to the molecular decomposition of diarenechromium with migration of energy and the formation of the corresponding multiplet states have been examined[2] (p.105). The formation of excited chromium atoms imparts surface activity to the solid phase formed, which is manifested by the autocatalytic character of the decomposition of dibenzenechromium, improved adhesion of the chromium segregated to the material of the support, and its increased adsorption capacity. The decomposition of the arene in the triplet state (for example, to a carbene) induces secondary reactions.[3]

The metals segregated (especialy W, Mo, Re, Cr, and V) are capable of being coordinated to olfefins, arenes, and carbenes, forming intermediate complexes which undergo further reactions,[3] leading ultimately to metal carbide structures.[101-103] For example, carbene complexes can disproportionate to a carbyne complex with a metal–carbon triple bond and further to methane and the $-M\equiv C-$ carbide species.

The possibility of the decomposition of the OMC triplet into a singlet molecule (toluene from diethylbenzenechromium) and a carbene complex of the metal via the scheme

$$(CH_3CH_2C_6H_5)_2M \rightarrow 2CH_3C_6H_5 + CH_2{:} \rightarrow M \leftarrow {:}CH_2 \rightarrow$$
$$\rightarrow CH_2{-}M\equiv CH \rightarrow CH_4 + {-}M\equiv C{-}$$

has not been ruled out.[3,64]

The heterogeneous decomposition of the OMC of *d* metals on the surface in accordance wit the spin conservation rule (an analogue of the Wigner rule) takes place on active centres (AC) having unpaired electrons.[3] Such centres may be absorbed metal atoms, whose role is similar to that of free radicals in the homogeneous decomposition.

The decomposition of ferrocene with formation of iron in the ground state is possible when triplet AC, which may be chemisorbed iron atoms, are present on the surface:[3,63]

$$Fe(C_5H_5)_2(S) + AC(T) \rightarrow (C_5H_5)_2(S) + Fe(^5D_4) + AC(T),$$

where S is the singlet, T the triplet, and $^5D_4$ the ground state of iron.

The chemisorbed iron atoms, which are effective dehydrogenation catalysts, promote the formation of iron-cross-linked polymers, which has been frequently observed experimentally.[25,97] By suppressing the dehydrogenation reaction by adding hydrogen, it has been possible to obtain α-iron from 1,1'-diethylferrocene,[57] nickel from nickelocene,[80] and ruthenium from ruthenocene.[2]

Either the chemisorption of atomic chromium, or the cleavage of the benzene ring, or the dehydrogenation of the latter are necessary for the retention of the multiplicity of the OMC–AC system in the heterogeneous decomposition of the diarene derivatives of chromium.[63] In the presence of a catalyst (iodine, bromine, and sulphur),[3] which removes the spin prohibition, the decomposition of diarene-chromium proceeds with segregation of pure chromium and ethylbenzene without the cleavage of the latter.

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The above analysis of the literature data revealed regularities in the variation of the kinetic parameters of the mechanism of the thermal decomposition of the test compounds as a function of the nature of the metal and the ligand and also the reaction conditions. The rate and mode of the thermal decomposition of the OMC investigated are determined by the nature of the reactant, mainly by its electronic temperature, the metal–ligand bond dissociation energy, and the ratios of this energy to the C–C and C–H bond dissociation energies in the ligand. Nor are there any grounds for the exclusion of the influence of steric factors on the kinetic thermal stability of the test compounds. The steric effect of the ligand on the stability of the complex, especially its quantitative aspect, have not been described in the literature. Nevertheless, in estimating the stability of the compound, it is essential to take into account also the steric effect together with the electronic influence.[104]

The decomposition reactions of the classes of comounds considered have not been found to be the same. A free radical pyrolysis mechanism via the homolytic cleavage of the metal–ligand bonds and the C–C and C–H bonds in the ligand has been proposed for mononuclear cyclopentadienyl compounds of transition metals. Predominantly molecular decomposition, involving the dissociation of the ring–metal bond or the elimination of a carbene and its stabilisation via coordination to the segregated metal and subsequent conversion of the carbene complex via known schemes, is characteristic of diarene compounds. The π–σ rearrangement, leading to the formation of radicals takes place to a slight extent in the decomposition of the diarene derivatives of metals.[105] It may be that the C–H bond dissociation process in the metallocenes is also preceded by the π–σ rearrangement, which has been detected for ferrocene by NMR.[106] However, from the standpoint of the conservation rules for the orbital symmetry and the total spin of the system, common features are observed in the radical and molecular mechanisms of the decomposition and also an analogy between the homogeneous and heterogeneous decomposition pathways.[3]

In recent years, a new field of study has begun to develop—the study of the adsorption of OMC and their volatile decomposition products on various surfaces, which determine the character of the interaction of the test compounds with the surface, and also the establishment of a correlation between the structure of the OMC and its adsorption capacity in relation to the metal-containing solid products of its own decomposition. However, these studies have only just begun, the range of compounds investigated is inadequate, and the nature of the adsorption complexes obtained has not been established. The importance of expanding the adsorption investigations is dictated by the fact that adsorption is one of the stages in the heterogeneous-catalytic decomposition which makes a definite contribution to the kinetics of the overall process.

In conclusion, it must be emphasised that the range of kinetic studies on the thermal decomposition of OMC is fairly narrow. Furthermore, the use of OMC is very promising in practice. The needs of modern technology for new materials in fact make it necessary to develop further the theoretical and experimental studies designed to determine the kinetics of the thermal decomposition of various OMC, whose knowledge is essential for the optimisation of the process leading to the formation of inorganic coatings and materials.

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Oxidative Chlorination of Aliphatic Hydrocarbons and Their Chloro-derivatives

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The problems of the thermodynamics, the selection of catalysts, and the kinetics and mechanisms of the oxidative chlorination reactions of aliphatic hydrocarbons and their chloro-derivatives and the technological arrangement in the reactor unit are considered in relation to C_1-C_3 hydrocarbons.
The bibliography includes 154 references.

CONTENTS

I. Introduction 326
II. Thermodynamics 326
III. Catalysts 327
IV. The kinetics and mechanisms of the oxychlorination reactions 329
V. The technology of the processes 332

I. INTRODUCTION

Oxidative chlorination (or oxychlorination) is the hydrocarbon chlorination reaction occurring with participation of an oxidising agent, which is usually oxygen. The chlorinating agent is as a rule hydrogen chloride, the need to use large amounts of which has in fact been the cause of the development of the oxychlorination method.

The oxychlorination of a wide range of hydrocarbons and their chloro-derivatives has been described in the literature. The oxychlorination is carried out in the gas phase in the presence of a heterogeneous catalyst and also in the melt and in a catalyst solution.[1-5] Since it is most widely used, attention is concentrated in the review on the first of the above procedures. A number of studies have been devoted to oxychlorination in salt melts,[6-9] while oxychlorination in solutions of catalytically active salts has been described in detail in recently published reviews[10,11] and dissertations.[12,13]

Many publications have been devoted to the gas-phase heterogeneous-catalytic oxychlorination of hydrocarbons and their chloro-derivatives, covering many aspects of this problem[14,15] or its individual aspects, such as the selection of catalysts and the mechanism of their action,[16,17] the kinetics and mechanisms of the reactions,[18] the relevant technology and economics, and a review of the patent literature.[19,20]

The present article is devoted to the consideration of the current state of the problems of the thermodynamics, the selection of catalysts, and the kinetics and mechanisms of the oxychlorination reactions as well as the technological arrangement for the processes, mainly in relation to C_1-C_3 hydrocarbons and their chloro-derivatives, since the fundamental questions of theory and practice have been dealt with in studies on the oxychlorination of these compounds.

In terms of the mechanism, all the oxychlorination reactions can be subdivided into two large groups: (1) reactions which proceed via the intermediate oxidation of hydrogen chloride by oxygen to chlorine, which chlorinates the organic substrate; (2) reactions which do not require the preliminary oxidation of hydrogen chloride to chlorine. The substitutional oxychlorination reactions of alkanes (and chloroalkanes) belong mainly to the first group, whilst the second group includes the additive oxychlorination reactions of alkenes (and chloroalkenes):

$$2HCl + 0.5O_2 \rightleftarrows Cl_2 + H_2O,$$

$$RH + Cl_2 \rightarrow RCl + HCl,$$

$$\rangle C{=}C\langle + 2HCl + 0{,}5O_2 \rightarrow \rangle \underset{Cl\ Cl}{C{-}C}\langle + H_2O \quad .$$

Gel'bshtein[18] placed the chlorination of alkenes in a separate group:

$$\rangle C{=}C\langle_{H} + HCl + 0.5O_2 \rightarrow \rangle C{=}C\langle_{Cl} + H_2O \quad .$$

The reaction takes place at temperatures at which hydrogen chloride is oxidised and alkanes undergo substitutional oxychlorination, but there is no chlorine in the gas phase. It may be that the reaction proceeds via additive oxychlorination with subsequent dehydrochlorination. The elimination of hydrogen chloride is observed in high-temperature oxychlorination.[13] The additive oxychlorination of alkenes occurs at temperatures up to 300 °C (there is virtually no oxidation of hydrogen chloride to chlorine under these conditions), while the substitution oxychlorination of alkenes and alkanes takes place at temperatures above 350 °C.[1,14,15]

Processes involving the oxidative chlorination of ethylene to dichloroethane[1,14,20] and of ethylene, propene, and their chloro-derivatives to carbon tetrachloride, trichloroethylene, and tetrachloroethylene[21,22] have found extensive industrial application. The development of an oxychlorination technology in melts of metal chlorides and oxide chlorides has also been reported,[23,24] but there has been no information about its practical exploitation, which indicates difficulties in the industrial application of such a process.

We shall consider the individual aspects of the oxychlorination reactions.

II. THERMODYNAMICS

The reversible oxidation reaction of hydrogen chloride (the Deacon reaction) is of greatest interest from the thermodynamic point of view. The problems concerning the thermodynamics of this reaction have been examined in fair detail in earlier reviews.[1,14] The constants K_p and the degrees of conversion of HCl and O_2 decrease appreciably with increase in temperature. According to Arnold and

Kobe's data,[25] the following expression relating lg K_p to temperature is valid in the temperature range 200–2000 °C: lg K_p = 5881.7/T–0.93035 lg T + 1.3704 × 10^{-4} T–1.758 × 10^{-8} T^2–4.1744, or in a simplified form: lg K_p = 6104.0/T–7.0994. When the Deacon reaction and the chlorination reaction take place simultaneously, the reaction equilibrium shifts as a result of the consumption of chlorine, which may entail the virtually complete conversion of hydrogen chloride.[1]

III. CATALYSTS

Numerous studies have been devoted to the selection of new and the improvement of existing catalytic oxychlorination systems.[1,14,15] They concern the question of the choice of the most active and selective catalytic compositions, carriers, and methods for the preparation of catalysts and the stabilisation of their operation. Despite a number of advances achieved on these lines, copper(II) chloride, proposed as the catalyst for the oxidation of hydrogen chloride as early as the XIXth century, still remains the main constituent of the catalysts for the Deacon and oxychlorination reactions.

It is most likely that hydrogen chloride is oxidised in accordance with Scheme 1, which includes copper reduction and oxidation stages:[26,29]

Scheme 1

$$2CuCl_2 \rightleftarrows Cu_2Cl_2 + Cl_2 \text{ (gas)},$$
$$Cu_2Cl_2 + 0.5O_2 \text{ (gas)} \rightleftarrows CuO \cdot CuCl_2,$$
$$CuO \cdot CuCl_2 + 2HCl \text{ (gas)} \rightleftarrows 2CuCl_2 + H_2O \text{ (gas)}.$$

It has been suggested[27] that a peroxy-compound is formed in the reaction with oxygen in order to account for the observed second-order of the reaction with respect to copper monochloride:

$$2CuCl_2 \rightleftarrows 2CuCl + Cl_2 \text{ (fast)},$$
$$2CuCl + O_2 \rightarrow Cu_2O_2Cl_2 \text{ (slow)},$$
$$Cu_2O_2Cl_2 + 4HCl \rightarrow 2CuCl_2 + Cl_2 + 2H_2O .$$

The direct interaction of bivalent copper chloride with oxygen is unlikely in view of the positive value of ΔG for this reaction.[18,26-29]

Gel'bshtein and co-workers[30-32] did not consider the decomposition of bivalent copper chloride with evolution of chlorine, assuming that chlorine is evolved in two steps: in the adsorption of oxygen and in its subsequent interaction with the adsorbed hydrogen chloride (Scheme 2):

Scheme 2

$$[Cu_mCl_n] + 2HCl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Cu_mCl_n \cdot 2HCl] \text{ (slow)},$$
$$[Cu_mCl_n \cdot 2HCl] + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [Cu_mCl_n \cdot 2HCl \cdot O_2] \text{ (slow)},$$
$$[Cu_mCl_n \cdot 2HCl \cdot O_2] + 2HCl \overset{k_3}{\rightleftarrows} [Cu_mCl_n] + Cl_2 + 2H_2O \text{ (fast)},$$
$$[Cu_mCl_n \cdot 2HCl] + Cl_2 \overset{k_4}{\rightleftarrows} [Cu_mCl_n \cdot 2HCl \cdot Cl_2] \text{ (fast)}.$$

One of the causes of the high catalytic activity of copper is its capacity for complex formation. It has been assumed that the interaction with oxygen does not go as far as the formation of copper oxide chloride but stops at the chemisorption stage. The oxidation reduction transformation of the copper cation in the Deacon reaction then proceeds in one stage – chloride ions transfer electrons to the absorbed oxygen via the copper cations, i.e. via a relay mechanism. Nevertheless, in the latest studies by the same workers[18,33] preference was given to the mechanism postulating the decomposition of $CuCl_2$ with evolution of chlorine.

The formation of univalent copper in catalytic systems has been established by the majority of investigators[26-29,33,34] and in many studies[26-29,33] the stages of Scheme 1 were investigated separately. Scheme 1 can serve as a good illustration of one of the first theories of catalysis, which explains the mechanism of the catalytic action by the formation of intermediate compounds, which are then converted into the reaction products with regeneration of the initial catalyst.

According to a series of data,[31,32,35-37] the first stage of the oxychlorination reaction of hydrocarbons, namely the oxidation of hydrogen chloride to chlorine, takes place at the same rate in the presence and absence of the hydrocarbon. Since the subsequent chlorination can proceed also without the participation of the catalyst, the main task in the development of a catalytic system for these reactions is the selection of the active component for the first stage.

Systems consisting of a carrier impregnated with copper chlorides and added chlorides of alkali, alkaline earth, lanthanide, and more rarely, other elements are most widely used as catalysts for the oxychlorination of methane.[38,39] A catalyst based on chromium oxide is also frequently employed.[40] An attempt has been made to combine the two familiar catalysts in the structure of the copper-chromium spinel $CuCr_2O_4$.[41,42] Catalysts based on iron[43] and its mixtures with copper, chromium, and alkali metals have also been described.[44] Rarer catalytic systems are also used: platinum, ruthenium, and potassium complexes on a carrier[45] and a mixture of palladium and lithium chlorides with added calcium, sodium, and potassium chlorides.[46]

The activities of the basic catalysts for the oxychlorination of methane enumerated above have been compared[42] and it has been shown that the most active catalyst is copper(II) chloride mixed with potassium and lanthanide chlorides. The attempts to bind copper in the spinel structure ($CuAl_2O_4$, $CuCr_2O_4$) and to use involatile copper compounds (CuF_2) were unsuccessful, since, under the conditions of an excess of hydrogen chloride and an elevated temperature, all these compounds are gradually converted into copper(II) chlorides.

It has been suggested[47] that copper be used in the form of the oxide, sulphate, nitrate, phosphate, stannate, plumbate, chromate, molybdate, vanadate, etc. in a mixture with compounds of the lanthanide elements. However, under oxychlorination conditions one may expect their gradual conversion into chlorides, so that the real catalytic system would not then differ from the traditional one.

Communications concerning the possibility of the oxychlorination of methane at relatively low temperatures (less than 200 °C) by using colloidal silicon dioxide as the carrier have appeared recently.[48-50] A salt melt without a carrier is frequently used for the oxychlorination of methane.[8,9,23,24,26]

It has been shown[15] that catalysts for the oxidative chlorination of ethane hardly differ from the systems used for the oxychlorination of methane.

Under the oxychlorination conditions, the mixture of the chlorides of copper, alkali metals, and a number of promoting agents is present as a rule on the carrier surface in the molten state.[1,14,15,30,35,51] It is noteworthy that the appearance of univalent copper in the system as well as the introduction into the latter of alkali metal chlorides reduces the melting point of the eutectic. This results in the formation of complexes having different chemical compositions[26-52] – $KCuCl_3$, K_2CuCl_4, K_2CuCl_3, and $K_2Cu_2Cl_6$. Lanthanide metal chlorides also greatly lower the melting point of copper(II) chloride.[53]

The melt of the active mass of copper and potassium chlorides on carriers of different chemical nature with different specific surfaces forms isolated inclusions having a thickness equivalent to 10–200 molecular layers in the extensive pore system of the carrier.[51,54,55]

Porous substances with a wide range of specific surfaces (from 0.5–1 to 200–500 $m^2\ g^{-1}$) are used as carriers.[1,14,15] The question of the selection of the carrier is fairly specific. As a rule carriers with larger surface areas are used to effect the process in a fluidised catalyst bed rather than with a stationary bed. This is because

coarsely porous carriers having a limited surface area, used to reduce the rate of side reactions, retain the melt poorly, which leads to the sticking together of the catalyst particles when reactors with a fluidised bed are employed and appreciably impairs the process parameters.[56,57]

It has been shown[30-32,35] that hydrogen chloride is oxidised in the bulk of the salt melt. Aglulin[35] believes that the chlorination proceeds, up to 425 °C, mainly via a heterogeneous mechanism on the surface of the salt melt, while at a higher temperature the process takes place predominantly via a heterogeneous–homogeneous pathway. Another worker[58] believes that the chlorination occurs mainly homogeneously in the gas phase.

An important factor in the choice of the oxychlorination catalyst is the minimisation of side reactions involving the extensive oxidation of alkanes and the oxychlorination reaction products (chloroalkanes) to carbon oxides. The side reaction is believed to be a catalytic process[58] and it is assumed that both the carrier surface free of the salt melt[54] and the surface of the salt inclusions[59] are responsible for the occurrence of this reaction.

It appears essential to consider the individual questions concerning the use of catalysts with copper chlorides in oxychlorination processes.

At the elevated temperature (250–500 °C) normally used for oxychlorination, copper chlorides are appreciably volatile: $\lg p(\text{mm Hg}) = -3550T^{-1} + 6.55$.[60] Carriers with various physicochemical properties are used and alkali metal chlorides forming complexes with the copper salt are introduced into the system[61] in order to reduce the volatity of the active components. All these procedures make it possible to lower by 1–2 orders of magnitude the volatility of copper and to form catalysts whose operation is stable.

The use of carriers and additives stabilising copper(II) chloride makes it possible, according to Kartashov et al.,[62] to retain the activity of the catalyst during 400–500 days of continuous operation. The problem of the loss of active components is especially acute when the process is carried out in a stationary bed where local superheating of the catalyst occurs. The volatilisation of copper chlorides can alter the catalyst selectivity as a function of time as a result of the change in the Cu:K ratio in the active salt mass.

Catalysts in which the copper cations are strongly adsorbed within zeolite pores[63,64] or are chemically bound in the catalyst structure (spinels)[41] are used to reduce the volatility of copper, but such catalysts have no advantages over the usual catalysts because of the gradual change in the catalyst composition under the influence of hydrogen chloride and the high temperature.[42,65]

The question of the influence of a number of other variable-valence metals on the catalytic activity of systems based on copper compounds is of great interest. These are in the first place iron, chromium, and nickel compounds, which have been patented as activators of the above catalytic system and individual oxychlorination catalysts[1,14,15] which can also be incorporated in the catalyst as a result of the metal exchange between the reactor surface and the catalyst.[66,67] The results of studies of the influence of these additives on the activity and stability of the operation of the catalyst based on copper chlorides are contradictory, especially as regards the iron compounds. In the oxidative chlorination of dichloroethane, the introduction of chromium, nickel, and iron chlorides into the catalyst increases the conversion of the reactants and raises the yield of the target products–trichloro- and tetrachloroethylenes[68]–by a factor of 1.5–2.

In the oxidative chlorination of methane,[69] there is a sharp increase in the yield of carbon monoxide in proportion to the increase in the content of iron(III) chloride in the catalyst. The degrees of conversion of methane and oxygen do not increase while that of hydrogen chloride diminishes, because hydrogen chloride is evolved in the combustion of chloromethanes. The introduction of chromium and nickel chlorides has almost no effect on the activity of the catalyst.

The most marked increase in the rates of the Deacon and substitutional oxychlorination reactions is observed when lanthanide chlorides are added to copper and potassium chlorides.[42]

Copper(II) chloride is the dominant catalyst in the additive oxychlorination reactions[1,14,15,19,70-72] which do not include the hydrogen chloride oxidation stage. The catalytic process can be illustrated schematically in relation to the oxychlorination of ethylene (Scheme 3):

Scheme 3

$$2CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + Cu_2Cl_2 ,$$
$$Cu_2Cl_2 + 2HCl + 0.5O_2 \rightarrow 2CuCl_2 + H_2O .$$

The formation of univalent copper has been confirmed by X-ray diffraction data for the catalyst.[73]

In view of the wide-scale industrial use of the oxidative chlorination of ethylene, the choice of the appropriate catalysts is of great practical interest. Almost all the catalysts include, apart from copper(II) chloride, various additives, which depend on the process temperature. Allen and Clark[16] showed that the activity of the catalyst for the oxychlorination of ethylene increases appreciably when yttrium chloride is added. The useful life of the catalyst also increases under these conditions. Alumina is used preferentially as the carrier, but activated charcoal, silica gel, aluminosilicate, zeolites, and other carriers can also be used.[1,14,15]

The oxychlorination of ethylene in the presence of the catalyst with copper(II) chloride deposited on different carriers, including alumina or activated charcoal, takes place at 210–280 °C and the yield of 1,2-dichloroethane is at the level of 99%.[15,17] An increase in temperature promotes the acceleration of the substitutional oxychlorination and dehydrochlorination, which results in the formation of considerable amounts of vinyl chloride, polychloroethanes, and di-, tri-, and tetra-chloroethylenes.[1,74]

The choice of the carrier is very important for the activity of the catalyst. On the basis of the analysis of literature data, it has been concluded[1,14,15,20] that the greatest activity in the temperature range 200–260 °C is shown by catalysts based on alumina. An increase in temperature lowers the selectivity in the formation of dichloroethane and even leads to the loss of activity by the catalyst. It has been shown[75-78] that the activity and selectivity of the action of the catalyst depend to a great extent on the phase composition of the alumina. The use of η- or κ-Al_2O_3 [77] leads to an almost 100% yield of dichloroethane at 200–240 °C. According to Flid et al.,[75] when the process is carried out in a "fluidised" catalyst bed, it is useful to employ microspherical alumina containing the α-, θ-, and γ-forms in the proportions 1:2:4.

The content of the θ-phase of Al_2O_3 in the carrier plays a major role. The deposited copper(II) chloride reacts with it to form copper aluminates with spinel structures. The copper then exists on the surface both as $CuCl_2$ and as hydroxide chlorides, whose structure depends on the carrier. It is claimed[78] that the increase in the activity of the catalyst is associated with the increase in porosity, the content of the θ-phase, and the number of basic centres on the carrier surface.

The question of the effect of catalyst poisons on the ethylene oxychlorination catalyst is of great practical importance.[79] This problem has so far been inadequately investigated, but there are data showing that the activity of the catalyst decreases when sulphur compounds enter this system.[80,81]

It is claimed[80] that the deactivation is associated with the formation of the inactive copper sulphate and hence with the decrease in the content of copper(II) chloride in the catalysts, which leads directly to a decrease in activity.

The authors of the present review hold another view. It has been established[81] from IR spectroscopic data that copper sulphate is not formed under the reaction conditions. The impairment of the process parameters is associated, in our view, with the reduction of Cu^{2+} to Cu^{+} by sulphur dioxide and the reduction of copper(II) chloride by ethylene, which competes with the above reaction, and also with the blocking by the sulphur-containing ions of the centres on the carrier surface participating in the reaction. It has been suggested that the surface sulphur-containing structures be removed in order to restore the activity of the catalysts.[81]

It is of great interest to carry out the oxychlorination of ethylene at elevated temperatures (350–500 °C). Under these conditions, the process is performed in the presence of catalysts with the traditional mixture of the catalytically active components. The main difference consists in the employment of carriers more resistant to the action of high temperatures than alumina. They include primarily silica gel, α-alumina, and celite.[82] The possibility of using catalysts containing lanthanide metal chlorides together with copper and alkali metal chlorides has been considered.[82] The selectivity in the formation of vinyl chloride in the oxychlorination of ethylene at such temperatures reaches 92%.[83] The employment of the $CuCl_2-KCl$ catalyst on silica gel and of the $FeCl_3-KCl-La_2O_3$ catalyst on celite at 500 °C makes it possible to achieve a yield of vinyl chloride up to 50%.[15] At lower temperatures (370–430 °C) and when the $CuCl_2-KCl-PrCl_3$ catalyst on microspherical silica gel is used, the main products are tri- and tetra-chloroethylene (selectivity up to 80%).[84]

Vinyl chloride can be obtained also at temperatures in the range 200–300 °C by using primarily catalysts containing platinum group metal compounds together with copper and iron.[15,20,85-87] The presence of copper and iron compounds in the catalyst is evidently essential for the oxidation of the platinum group metals (Scheme 4):[87]

Scheme 4

$$C_2H_4 + PdCl_2 \rightarrow C_2H_3Cl + Pd + HCl\ ,$$
$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl\ .$$

The method of preparation of the catalyst has a great influence on its properties, including the selectivity and stability of its operation.[87] It has been established in the synthesis of the $Pd-Fe/Al_2O_3$ catalytic system that the optimum stability of operation of the catalyst is observed when the α- and θ-forms are present in the Al_2O_3,[87] which agrees with the data on the low-temperature oxychlorination described above.

The catalyst activity series for the formation of vinyl chloride is Pd > Rh > Pt > Ru; the highest selectivity has been achieved using palladium. A disadvantage of the catalysts described is the limited conversion of ethylene.

The main pathway in the oxychlorination of chloroethanes and chloroethylenes involves the formation of tri- and tetra-chloroethylenes.[1,15,20] The oxychlorination of chloroethylenes can be carried out in the presence of the catalyst described above at 200–300 °C and involves the addition of chlorine to the double bond.[1,88] An increase in the oxychlorination temperature to 400 °C makes it possible to obtain also tri- and tetra-chloroethylenes with fair selectivity (to an extent greater than 80%).[84,88] Tetrachloroethylene also can be obtained[89] by oxidising tetrachloroethane or other chloroethanes with a high chlorine content at 390 °C in the presence of the traditional oxychlorination catalyst.

Under the conditions of the high-temperature oxychlorination of chlorohydrocarbons of the ethane–ethylene series, the carrier has a much smaller influence on the properties of the catalyst. This applies especially to the process in a stationary catalyst bed. It has been shown[90] that the use of carriers greatly differing in chemical composition (Al_2O_3, SiO_2, $Al_2O_3-SiO_2$) and also in the specific surface and porosity in the oxychlorination of 1,2-dichloroethane leads to similar results as regards the conversion of the reactants and the selectivity in the formation of the target products.

Two main pathways must be distinguished in the oxychlorination of C_3 hydrocarbons: the synthesis of allyl chloride from propene and of organochlorine solvents (tri- and tetra-chloroethylenes, carbon tetrachloride) from different types of raw material.

In in the oxychlorination of propene in the temperature range 150–350 °C in the presence of the copper-based catalyst, the main product is 1,2-dichloropropane.[1,14,15,91] An increase in temperature leads to the appearance of appreciable amounts of allyl chloride in the products, but it also greatly accelerates the extensive oxidation side reactions and the loss of copper.

The principal procedure for increasing the selectivity in the formation of allyl chloride at relatively low temperatures (150–300 °C) involves the use of catalysts containing compounds of platinum group metals and tellurium. The possibility of the selective formation of allyl chloride at 180–240 °C in the presence of a catalyst containing platinum group metals on a carrier has been indicated.[90] The catalytic activity of the metals varies as follows: Rh > Pd > Pt > Ir > Ru; activated charcoal is the best carrier. It has been shown that the use of a mixture of platinum group metal, copper, and lanthanide chlorides[15,87,92] greatly increases the rate of reaction. The selectivity in the formation of allyl chloride reaches 90%. The mechanism of the action of the catalyst is analogous to that described for ethylene (see Scheme 4). The presence of platinum group metals in the catalyst virtually rules out the formation of 1,2-dichloropropane and the main side product is isopropyl chloride. The stability of the operation of this catalytic system is ensured by alkali metal chlorides, the best of which is sodium chloride[87,92] which does not impair the selectivity of action of the catalyst.

The use of tellurium compounds ensures a selectivity in the formation of allyl chloride at the level of 90% and above.[93] The presence of alkali metal chlorides lowers the selectivity and it is desirable that the catalyst should contain platinum group metal compounds in order to increase it.[94]

The oxychlorination of C_3 hydrocarbons and their chloro-derivatives is frequently carried out in order to obtain organochlorine solvents, traditional and modified catalytic systems being used for this purpose at temperatures which are as a rule above 350 °C. The reaction product consists of a complex mixture of hydrocarbons, the target products being tri- and tetra-chloroethylenes and carbon tetrachloride.[13,63,95]

IV. THE KINETICS AND MECHANISMS OF THE OXYCHLORINATION REACTIONS

It has been established in the course of a whole series of investigations[18,31,35,36] that the high-temperature oxychlorination proceeds via a stage involving the oxidation of hydrogen chloride to chlorine. The mechanism of the oxidation of HCl was described in the Section dealing with the catalysts and the kinetics of this reaction have been fairly well investigated.[18,29,30,etc] One can only state that the probabilities of the possible type of mechanisms of this reaction have been estimated[18] in accordance with the available experimental data.

Despite the definite differences between the postulated mechanisms of the Deacon reaction and even the disagreement concerning the region where it occurs (on the surface or in the bulk of the melt),[27,29,35] the rate of reaction r is described in all cases by equations of the following type after some simplification:

$$r = \frac{k\, p_{O_2}}{p_{Cl_2}}\ .$$

Until recently, the kinetics and mechanism of the oxychlorination of methane had been little investigated. It was established[96] that the chlorination of methane in the melts occurs at higher rates than the thermal process, the authors suggested that this takes place as a result of the iniation of the gas-phase process by the chlorine atoms evolved from the surface of the melt. This view was questioned[97] on the grounds that the rate of evolution of chlorine in the thermal decomposition is much lower than the rate of chlorination and also because of the difference between the selectivities in the gas-phase and catalytic chlorinations. This suggests that the chlorination of methane takes place predominantly directly in the melt.[97]

Other workers,[18,31,32,35] who have studied the kinetics and mechanism of the methane oxychlorination reaction in greatest detail, hold an analogous view. It has been shown that the oxidation of HCl takes place throughout the bulk of the melt with participation of $CuCl_2$ (see Scheme 2) regardless of the subsequent chlorination of methane, which is indicated by the same kinetics being observed when the reaction is studied in the presence and absence of methane.

It is believed[31,32,35] that the chlorination of methane up to 425 °C takes place on the surface of the melt predominantly via the interaction of methane with a polyhalide complex of the type ZCl_3, formed when molecular chlorine is chemisorbed by metal chlorides, Z being the free catalytic centre:

$$ZCl + Cl_2 \rightleftarrows ZCl_3 (ZCl \cdot Cl_2) ,$$

$$ZCl_3 + RH \rightleftarrows RCl + HCl + ZCl .$$

An increase in temperature increases the contribution of the reaction involving the thermal bulk-phase chlorination by free chlorine. It has been concluded[35] that the melt-free catalyst surface is virtually uninvolved in the chlorination reaction. The hypothesis has been put forward that metal chlorides inhibit the reaction in the bulk phase because of their greater affinity for chlorine.

Since the rate and kinetics of the chlorination of methane depend little in practice on the changes in the composition of the $CuCl_2-KCl$ system, the introduction of $LaCl_3$, or the replacement of $CuCl_2$ by LiCl, the authors suggest that the participation of variable-valence metal chlorides in complexes of the type ZCl_3 ($ZCl.Cl_2$) is not obligatory and that chlorination can take place on catalytic centres different from those which are essential for the oxidation of HCl.

The reactions involving the oxidative and direct chlorination of methane in the presence of salt catalysts are described by the same kinetic equation,[31,32,35] i.e.

$$r = k p_{CH_4} p_{Cl_2}^{0.6} p_{O_2}^{n} ,$$

in which the order with respect to oxygen (n) varies with temperature from 0 to -0.25. Depending on the nature of the salt, the observed activation energy varies from 84 to 113 kJ mol^{-1}.

The use of semiconductor detector, mass-spectrometric, and molecular beam methods enabled Gel'bshtein and Bakshi[98] to justify the hypothesis of the heterogeneous-homogeneous character of the chlorination stage in the substitutional oxychlorination of alkanes.

The main side products in the oxychlorination of methane are carbon oxides. The rate of oxidation of methane and its chloro-derivatives is characterised by being first order with respect to the organic substrate and oxygen, while the ratios of the rates are $r(CH_3Cl) : r(CH_2Cl_2) : r(CHCl_3) : r(CH_4) : r(CCl_4) = 1 : 0.5 : 0.33 : 0.18 : 0.033$. The selectivity in the formation of CO increases with increase in the partial pressure of HCl.[32,35] The mechanism of the extensive oxidation reactions has been scarcely investigated.

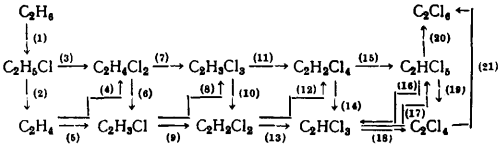
The occurrence of the partial oxidation reactions of chloroethanes and chloromethanes as well as the formation of condensation products (carbon black formation) has been indicated in most studies. It has been established[99] that, at elevated temperatures in the absence of oxygen, carbon is deposited on the catalyst in the decomposition of chloromethanes. In the normal course of the process, the decomposition of condensation products were burnt off by oxygen with formation of oxides, which agrees with Mamedov's data.[63]

The kinetics of the oxychlorination of methane in the presence of the spinel copper–chromium catalyst have been described[100] and an equation has been obtained for the overall rate: $r = k p_{CH_4}^{0.8} p_{O_2}^{0.4}$, with an activation energy of 155 kJ mol^{-1}.

The kinetics and mechanism of the high-temperature oxychlorination of ethane, propane, and their chloro-derivatives have been studied in less detail because of its much greater complexity compared with the oxychlorination of methane. Only the formation of chlorine and its involvement in the reactions of the hydrocarbons are unquestionable.[1,15,36,37,98] According to the results of Gel'bshtein and Bakshi,[98] the chlorine formation and chlorination reactions take place on different active centres.

When account is taken of the subsequent reactions of the intermediates, the oxidative chlorination of ethane consists of a heterogeneous-homogeneous process, which proceeds via a series of parallel-consecutive chlorination and dehydrochlorination stages and is accompanied by the oxidation of the starting materials and intermediates to carbon oxides. The simplified mechanism of the formation of the reaction products can be represented as follows (Scheme 5):[36,37,101]

Scheme 5



Depending on the conditions, the process can be directed towards the formation of chloroethylene (vinyl chloride) or towards more chlorinated products.

In view of the large number of individual reactions, the oxychlorination of ethane has been studied in stages. The observed rates of reaction of ethylene, ethane, chloroethane, 1,2-dichloroethane, chloroethylene[36,37] and also the rates r_{16}, r_{18}, and r_{19} [106] are described satisfactorily by the equation

$$r_i = k_i p_i p_{Cl_2}^{0.5} . \qquad (I)$$

The rates of reaction of 1,1-dichloroethane depend solely on its partial pressure.

The following reaction pathways in Scheme 5 have been discovered:[18,56,57,102] (a) chloroethane is converted into 1,1-dichloroethane, 1,2-dichloroethane, and ethylene; (b) 1,2-dichloroethane is converted into 80% chloroethylene and 20% 1,1,2-trichloroethane; (c) ethylene, chloroethylene, and dichloroethylene are chlorinated only additively; (d) chloroethylene is formed as a result of the dehydrochlorination of both dichloroethanes; (e) 1,1,2-trichloroethane is formed from chloroethylene and 1,2-dichloroethane but not from 1,1-dichloroethane.

It has been shown[103] that the oxychlorination of ethylene and chloroethylene take place with participation of the catalyst. Ethane, chloroethane, and 1,2-dichloroethane react with molecular chlorine via a radical-chain mechanism, while the dehydrochlorination of 1,1-dichloroethane and the dissociation of chlorine into atoms take place with participation of the catalyst.[104]

According to some data,[105,106] 1,1,2-trichloroethane is formed via both 1,2-dichloroethane and via chloroethylene, while the relative contributions of these pathways depend in the first place on the volume of the gas phase in the reactor.[106]

The observed rate constant in Eqn. (I) depends on the nature of the organic substrate and decreases in the sequence $C_2H_6 > C_2H_5.Cl > C_2H_4Cl_2$ for saturated compounds. The activation energies for the conversion of the saturated (130 kJ mol^{-1}) and unsaturated

compounds (40–90 kJ mol^{-1}) differ very markedly, as a result of which the yield of alkenes increases with increase in temperature.

In the oxychlorination of hydrocarbons of the ethane–ethylene series, extensive formation of carbon oxides takes place. The rates of these reactions described [36,37] by the empirical equation

$$r_{CO+CO_2} = k_i p_i p_{O_2} p_{Cl_2}^{0.5} \quad .$$

The main contribution to the formation of carbon oxides comes from unsaturated compounds.[6,37,87,89] The introduction of one chlorine atom into ethylene increases the observed extensive oxidation rate constant by a factor of 7–8, while further increase in the chlorine content in the molecule diminishes the degree of combustion of chloroalkenes.[36,37]

The kinetics and mechanism of the high-temperature oxychlorination of C_3 chloroalkanes, which proceeds with formation of tri- and tetra-chloroethylenes and carbon tetrachloride, have been investigated.[13,63,95] In the oxychlorination of 1,2-dichloropropane by the $Cl_2 + O_2$ mixture in the temperature range 310–390 °C in the presence of the $CuCl_2$–KCl catalyst on a carrier, it has been established[13] that the rates of decrease in the amounts of all the reactants are described by the general equation

$$r = k_i p_{C_3H_6Cl_2}^{0.7} p_{Cl_2}^{0.3} (1 + p_{O_2}) \quad .$$

It has been suggested that the reaction take place both in the bulk phase and on the catalyst, which agrees with the results of studies on the high-temperature oxychlorination of ethane, ethylene, and their chloro-derivatives presented above.

The additive oxychlorination of alkenes takes place on catalysts with $CuCl_2$ at much lower temperatures (200–300 °C) than the oxychlorination of alkanes and does not involve the HCl oxidation stage (see Scheme 3). The kinetics of the oxychlorination of ethylene and propene have been studied on a series of catalysts under different conditions and have been described in detail in several reviews.[1,14,15,20,107] The empirical equations proposed for the reaction rates differ appreciably depending on the catalyst and the process conditions.

The first kinetic study of the oxychlorination of ethylene was carried out[108] on the $CuCl_2$–Al_2O_3 catalyst at 200–300 °C. The authors claimed that the rate of the process is independent of $p_{C_2H_4}$ but does depend on p_{O_2} and also that the reaction is inhibited by dichloroethane and HCl. In subsequent investigations, these conclusions were not in the main confirmed. It was found[107,109] that the rate of reaction depends in a complex manner on the partial pressures of ethylene, HCl, and oxygen and is described by a power equation of the type

$$r = k\, p_{C_2H_4}^{m} p_{HCl}^{n} p_{O_2}^{l} \quad . \qquad \text{(II)}$$

In the presence of the $CuCl_2$–KCl/silica gel catalyst in the region of limited conversions of ethylene, the parameters in Eqn. (III) are $m = 0.6$, $n = 0.2$, and $l = 0.5$. In the presence of a catalyst based on Al_2O_3 a direct dependence of the rate $p_{C_2H_4}$ and p_{O_2} ($m, l = 1$) and a weak dependence on p_{HCl} ($n = 0.3$) in the region of low oxygen pressures have been established; when $p_{O_2} \geqslant 0.01$ MPa, we have $l = 0$. An analogous picture ($m = 1$, $n = 0.2$, and $l = 0$) is observed when the $CuCl_2$/activated charcoal catalyst is used in the temperature range 130–180 °C; the selective formation of dichloroethane is possible only under the conditions of an excess of ethylene.

On the other hand, it has been stated[109] that, when an Al_2O_3-based catalyst is used, the rate of reaction depends on $p_{C_2H_4}$ and p_{O_2} but is independent of p_{HCl}, which is evidence, according to the authors, that the rate of reaction is limited by the stage involving the interaction of ethylene with oxygen on the catalyst surface.

The most complete idea about the kinetics and mechanism of the additive oxychlorination of alkynes has been put forward in studies by Gel'bshtein and co-workers.[110-112] The addition to the catalyst of alkali metal chlorides, capable of being coordinated to the copper cation as well as the adsorption of hydrogen chloride increase the electron density on the copper cation and thereby increase the dative component in the interaction of the copper cation with the olefin and at the same time weaken the Cu–Cl bond. The dissociation of two such bonds results in the addition of chlorine atoms to the olefin and in the corresponding reduction of the copper cation in the active centre.

The following mechanism of the reactions (Scheme 6) has been proposed for the oxychlorination of ethylene (at 250–340 °C in the presence of the $CuCl_2$–KCl catalyst on aluminosilicate or silica gel):[110,111]

Scheme 6

		(A)	(B)
$[Cu_mCl_n] + HCl \rightleftarrows [Cu_mCl_n \cdot HCl]$	(1′)	1	1
$[Cu_mCl_n \cdot HCl] + HCl \rightleftarrows [Cu_mCl_n \cdot 2HCl]$	(1″)	1	0
$[Cu_mCl_n \cdot 2HCl] + C_2H_4 \rightarrow [Cu_m^{2-}Cl_{n-2} \cdot 2HCl] + C_2H_4Cl_2$	(2)	1	0
$[Cu_m^{2-}Cl_{n-2} \cdot 2HCl] + O_2 \rightarrow [Cu_mCl_{n-2} \cdot 2HCl \cdot O_2^{2-}]$	(3)	1	0
$[Cu_mCl_{n-2} \cdot 2HCl \cdot O_2^{2-}] + C_2H_4 + 2HCl \xrightarrow{\text{fast}} [Cu_mCl_n] + C_2H_4Cl_2 + 2H_2O$	(4)	1	0
$[Cu_mCl_n \cdot HCl] + C_2H_4 \rightleftarrows [Cu_mCl_n \cdot HCl \cdot C_2H_4]$	(5)	0	1
$[Cu_mCl_n \cdot HCl \cdot C_2H_4] + O_2 \xrightarrow{+2O_2} [Cu_mCl_n] + 2CO_2 + 2H_2O$	(6)	0	1

$2C_2H_4 + 4HCl + O_2 \rightarrow 2C_2H_4Cl_2 + 2H_2O$ (A)

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ (B) .

The numerals designating the stages and the stoichiometric numbers of these stages via pathways (A) and (B) are indicated to the right of the chemical equations.

If it is assumed that stages (1′), (1″), and (5) of Scheme 6 correspond to equilibrium, then the kinetic equations corresponding to the proposed Scheme and describing the rates of formation of 1,2-dichloroethane (r_A) and carbon dioxide (r_B) are as follows:

$$r_A = 2\,\frac{K_1' K_1'' k_2 p_{HCl}^2 p_{C_2H_4}}{1 + K_1' p_{HCl}\left[1 + K_5 p_{C_2H_4} + K_1'' p_{HCl}\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)\right]}, \qquad \text{(III)}$$

$$r_B = \frac{K_1' K_5 k_6 p_{HCl} p_{C_2H_4} p_{O_2}}{1 + K_1' p_{HCl}\left[1 + k_5 p_{C_2H_4} + K_1'' p_{HCl}\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)\right]} . \qquad \text{(IV)}$$

On the assumption that

$$K_1'' p_{HCl} \gg 1 + K_5 p_{C_2H_4}$$

Eqn.(III) assumes the form

$$r_A = 2\,\frac{K_1 k_2 p_{HCl}^2 p_{C_2H_4}}{1 + K_1 p_{HCl}^2\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)} ,$$

where

$$K_1 = K_1' K_1''$$

On the same assumption, Eqn. (IV) can be written in the form

$$r_B = \frac{K_1' K_5 k_6 p_{HCl} p_{C_2H_4} p_{O_2}}{1 + K_1 p_{HCl}^2\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)} .$$

Under conditions where $p_{O_2} \geqslant (p_{O_2})_{min}$ and $p_{HCl} \geqslant (p_{HCl})_{min}$, the rate of reaction is described by a simple first-order equation with respect to ethylene: $r = k_{obs} p_{C_2H_4}$.

The oxychlorination reaction of ethylene in the $CuCl_2$–KCl/γ-Al_2O_3 catalytic system has been investigated in detail.[113] The authors established that the maximum rate of formation of dichloroethane in the temperature range 220–300 °C corresponds to

a copper concentration in the catalyst of ~7.5%. The rate of formation of side products, in particular of ethyl chloride, CO, and CO_2, falls sharply with increase in the copper concentration. Kinetic studies confirmed the inhibition of the CO and CO_2 formation reactions by hydrogen chloride. It has also been shown that an increase in the Cu/K ratio lowers the activation energy for the dichloroethane formation reaction.

The kinetics of the oxychlorination of ethylene on the $PdCl_2-FeCl_3/\gamma\text{-}Al_2O_3$ catalyst at 230–280 °C have been studied.[87] The main products are chloroethylene and chloroethane whose rates of formation are described by Eqns. (V) and (VI):

$$r_{C_2H_3Cl} = k\, p_{C_2H_4}^{0.9}\, p_{O_2}^{0.6}\ , \qquad (V)$$

$$r_{C_2H_5Cl} = k'\, p_{C_2H_4}^{0.5}\, p_{HCl}^{0.8}\, p_{O_2}^{0.6}\ . \qquad (VI)$$

Analysis of Eqns. (V) and (VI) shows that chloroethylene and chloroethane are formed on different catalytic centres, since the orders with respect to HCl and C_2H_4 are different for these reactions.

The presence of zerovalent palladium and Fe^{2+} in the catalyst leads to an appreciable increase (by a factor of 2–3) in the degree of chemisorption of O_2. Evidently the catalyst surface is occupied by the palladium–iron complex with chemisorbed oxygen on which the main reaction products are in fact formed, which explains the identical reaction orders with respect to oxygen in Eqns. (V) and (VI).

The picture is similar in the oxychlorination of propene. The rate of reaction depends on the concentration of Pd and $PdCl_2$ in the catalyst and also on $p_{C_3H_6}$.[114] The kinetics of the oxychlorination of propene to 1,2-dichloropropane on the $CuCl_2-KCl/Al_2O_3$ catalyst have been studied.[112] The principal features are analogous to those obtained for ethylene. The rate of reaction at $p_{HCl} \geqslant 2$ kPa is described by the equation

$$r = k' p_{C_3H_6} \Big/ \left(1 + \frac{k' p_{C_3H_6}}{k'' p_{O_2}}\right)\ .$$

Depending on the conditions, the rate of the reaction is first order with respect to propene with an activation energy in the range of 90 kJ mol^{-1} or first order with respect to oxygen with an activation energy at the level of 30 kJ mol^{-1} (for zero reaction orders with respect to the other reactants).

V. THE TECHNOLOGY OF THE PROCESSES

This Section deals mainly with questions concerning the oxychlorination reactor—the most complex unit in the process.

In industrial practice the oxychlorination is carried out in different reactors,[1,14,15,20] for example on fluidised,[115, 116] and stationary catalyst beds,[117] and also in melts.[73] A highly isothermal process can be achieved in a fluidised bed, but, when the latter is employed, considerable complications arise in connection with the recovery of the catalyst, the corrosion of the heat exchange elements, the low conversion of the reactants, and the poor susceptibility to modelling. In reactors with a stationary bed considerable local superheating can occur, which leads to vigorous side reactions involving extensive oxidation. They are distinguished by an appreciably lower productivity but make it possible to achieve a high conversion of the reactants.[117,118]

The use of a combination of reactors with a fluidised bed (the first in the set-up for the process) and a stationary bed makes it possible[119] to create a set-up with a high productivity and a high conversion of the reactants.

Comparative study of the oxychlorination of methane in reactors with fluidised and stationary catalysts and also in the melt showed[120] that satisfactory results can be achieved under certain conditions.

When reactors with a fluidised catalyst bed are used, much attention is devoted to the conditions governing the fluidisation and mixing of the reactants. In order to eliminate the influence of backmixing and breakthrough in the form of bubbles, it was recommended that the reactor diameter be restricted to 100–500 mm,[121] which ensures minimal combustion as a result of uniform fluidisation without gas bubbles. In order to create set-ups with a high unit productivity, several tubes of this diameter are combined in a single jacketed tubular reactor. The removal of heat in the reactors is achieved with the aid of heat exchange elements[122] or by recycling the products.[123] To prevent the possibility of the decay of the reaction, it is recommended that the temperature of at least some of the heat exchange elements should differ from the temperature of the bed by not more than 25 °C.[122] Satisfactory mixing of the reactants promotes an increase in selectivity and is carried out directly in the fluidised bed,[115] in pre-mixers with a fluidised bed of inert materials,[124] or in special devices with a wide variety of designs.[125]

The oxychlorination stage is used mainly to establish processes, balanced with respect to chlorine, in which organochlorine products are obtained. The high-temperature chlorination is usually carried out in the first stage, while the hydrogen chloride from the chlorination stage is supplied to the oxychlorination stage, the products being either isolated from the reaction gas[126] or also supplied to the oxychlorination stage.[127] The supply to the oxychlorination stage of the same hydrocarbon raw material as in the chlorination stage is economically most efficient, since in this case there are no problems with the purification of hydrogen chloride.

Oxychlorination with a mixture of chlorine and oxygen or air is also known.[1,13,14,20,21,63,128,129] In this case the chlorination and oxychlorination reactions are combined in a single reactor; when polychlorides with a high chlorine content are processed under the conditions of a low heat change, this procedure is especially advantageous. Oxychlorination using chlorine takes place more vigorously, but, when C_2 and C_3 polychlorides are used, the contribution by extensive oxidation side reactions increases, in the first place owing to dehydrochlorination and the formation of alkenes which exhibit an increased tendency towards the formation of carbon oxides.[92,116] The yield of oxides is reduced by the means of an oxygen supply divided into sections along the height of the reactor[13,95,116,128,129] as a result of which the oxygen comes into contact not with the initial raw material but with more chlorinated hydrocarbons. The oxychlorination with a $Cl_2 + O_2$ mixture is carried out in reactors of all types, although it is assumed that the preferred variant involves the process being carried out in a pseudofluidised catalyst bed or in the melt.[13,128,129]

Processes in which hydrogen chloride is used have become the most common. There is also a possibility of employing hydrochloric acid.[130,131] The presence of large amounts of water vapour in the reaction mixture makes it possible to carry out the process successfully in a stationary bed—there is virtually no superheating of the catalyst in this case.[131] However, an excess of water vapour can also lead to the occurrence of side reactions. Thus reactions involving the formation of allyl alcohol, acrolein, and other oxygen-containing products are appreciably accelerated in the case of propene.[132] The interaction of chloroethylene with water vapour to form ethylene has been observed at temperatures above 450 °C.[133]

Air, air enriched in oxygen, and concentrated oxygen can be used as oxidants for oxychlorination.[128,129,134,135] The replacement of air by oxygen can greatly increase the productivity of the reactors, can simplify the condensation scheme by increasing the concentrations, and ultimately can reduce the intrinsic cost of the products. Under conditions where oxygen is used, the requirements for the removal of heat and conditions free from the risk of explosion become much more stringent, so that it is recommended that a reactor with a

fluidised catalyst bed be used for this purpose.[21,22,134,135] However, the possibility of the successful employment of concentrated oxygen also in reactors with a stationary bed has been demonstrated.[128,129] Provided that the conditions are chosen correctly, the selectivity in the formation of the target products is at the same level as in the case where air is used.

Oxidative chlorination has been used much less than the chlorination method because of the following disadvantages: (1) the volatility of the active components of the catalyst; (2) the formation of extensive oxidation side products ($CO + CO_2$) and the insufficiently high conversions of the reactants and yields of the target products (especially in the high-temperature process); (3) the pronounced corroding effect of the medium (catalyst, hydrogen chloride, chlorine, and water vapour at a high temperature).

The loss of copper(II) chloride from the catalyst is compensated by passing the initial reaction mixture through a melt or solid carrier containing copper(II) chloride.[136] When the oxychlorination is carried out in a fluidised bed, a constant amount of the catalyst is maintained by adding the solid carrier, copper in the form of the metal or a salt, and also an alkali metal as the chloride.[137]

In order to reduce the yield of carbon oxides and to improve the selectivity in the formation of target products, attempts are made in the first place to achieve the optimum temperature conditions in the oxychlorination reactions. It is recommended that the process be carried out in the presence of a (5–20)-fold excess of hydrogen chloride to maintain a uniform temperature in the catalyst bed.[138]

The attempts to organise temperature fields in reactors with a stationary catalyst bed by arranging the catalyst in order of increasing activity along the gas stream,[139] by a stepwise increase in the size of the catalyst particles,[140] and by increasing the tube diameter or by means of a higher temperature in each successive (along the gas stream) catalyst bed[141] are noteworthy.

The uniform mixing of active and low-activity catalysts increases[142] the yield of the target product by increasing the selectivity of the main reaction. The procedures described activate the process in the terminal part of the reactor and make it possible to achieve a high conversion of HCl.

It is also recommended that the catalyst be diluted by an inert material with a high thermal conductivity: graphite,[143] silicon carbide,[144] metals (nickel, molybdenum, cobalt, and silver) and their alloys,[145] and also the unimpregnated carrier.[146]

Only chloromethanes are recycled in the chlorination stage and only methane, oxygen, nitrogen, and carbon oxides are recycled in the oxychlorination stage in order to increase the degree of the useful employment of chlorine and to reduce the formation of side products.[147]

The greatest effect in reducing the extensive oxidation side reaction can be achieved by preventing contact between the hydrocarbon and oxygen by carrying out the process in two stages. In the first stage, the hydrocarbon is chlorinated with the aid of, for example, copper chloride, while in the second stage the reduced form of copper is oxidised by oxygen and hydrogen chloride. A melt of copper and potassium salts is usually employed to achieve such a process.[23,24,120,148] The low conversion of the hydrocarbons and the complexity of the equipment for transporting the melt should be included among the disadvantages of this method. In order to simplify the transfer of the catalyst from one stage to the other, it is suggested[149] that the traditional catalyst with $CuCl_2$ on a carrier be used. However, the formation of carbon oxides cannot be fully avoided even when a two-step scheme is used, since the oxidised form of the catalyst, coming into contact with the hydrocarbon, contains copper oxide chloride, which leads to the formation of carbon oxides.

Attempts have been made to reduce the corroding effect of the catalyst on the reactor material by selecting appropriately the carrier and the composition of the active mass,[150] but these improvements are not of fundamental importance. It has therefore been suggested that, when the process is carried out in a stationary bed, the surface of the tube should be coated with glass[140,151] or that a lined adiabatic reactor be employed.[152]

A procedure in which the oxychlorination process is initiated by means of a correct sequence in the supply of the reactants to the catalyst heated beforehand has been patented.[153] A method for the elimination of iron(III) chloride from the initial reactants[154] in order to maintain the activity and selectivity of the oxychlorination catalyst based on copper chlorides has also been proposed.

The above improvement in the technological set-up for the process permits the expectation of an expansion in the employment of the oxychlorination method at the present.

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Stable Methylenequinones

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Data obtained in studies on the chemistry of a vigorously developing class of conjugated compounds (methylenequinones) are surveyed. The structure of these compounds and the influence of substituents on their properties and reactivity are discussed. Typical methods of synthesis of methylenequinones are described and the mechanism of their formation as well as the interconversions of methylenequinones and the corresponding phenols in radical and heterolytic reactions are considered. The bibliography includes 144 references.

CONTENTS

I. Introduction 336
II. Structure, stability, and physicochemical properties 336
III. The formation of methylenequinones 338
IV. Radical reactions of methylenequinones 340
V. Heterolytic 1,6-addition reactions 342
VI. Isomerisation of methylenequinones 346

I. INTRODUCTION

Methylenequinones (quinone methides) are labile organic compounds belonging to the class of unsaturated cyclic conjugated ketones. The study of the properties of these substances has developed vigorously during the last decade primarily owing to the specificity of their structure, high reactivity, and the role which they play in many chemical and biochemical reactions.[1-3] Methylenequinones form part of the composition of plant pigments,[4] participate in the metabolism of natural products,[5] are used in medicine,[6] and are able to inhibit the thermo-oxidative degradation reactions of polymers.[7] Finally, the chemical properties of methylenequinones and phenols proved to be indissolubly linked, which is manifested most distinctly in the relation between sterically hindered phenols and the corresponding methylenequinones.[8]

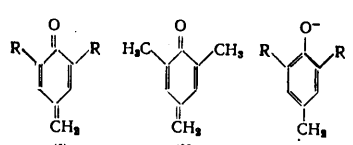
The molecules of methylenequinones are characterised by a high degree of conjugation, lability of the π-electronic bond system, and the capacity for the delocalisation of electrons, which is reflected in the physical properties of methylenequinones and in the marked influence of substituents, particularly those attached to the carbon atom of the methylene unit, on the structure and chemical properties of compounds of this class. This review deals with the methods of synthesis and the properties of stable *para*-methylenequinones.

II. STRUCTURE, STABILITY, AND PHYSICOCHEMICAL PROPERTIES

The simplest methylenequinones are usually unstable. Hitherto they have not been isolated in a pure state. At the instant of formation, these methylenequinones either polymerise or interact with the medium. Their high reactvitiy is due primarily to the characteristic features of their structure. Analysis of calculated data on the structure of the simplest methylenequinones and their closest analogues—quinones and dimethylenequinones (quinodimethanes)—has shown that the ground state of methylenequinones can be both singlet and triplet.[9] The triplet states of *p*-dimethylenequinone and *p*-methylenequinone are biradicals of the dibenzyl or hydroxybenzyl type with a benzenoid (and not quinonoid) aromatic ring and one can therefore speak of the ground singlet (quinonoid) state of these conjugated compounds and of their transition triplet (benzenoid) state. Calculations on the singlet and triplet states of the *p*-dimethylenequinone molecule have shown[9-11] that in the former case it is diamagnetic and has a quinonoid structure, while in the latter state the molecule should be paramagnetic and should have a benzenoid structure with similar C–C bond lengths in the six-membered ring. The difference between the energies of the singlet and triplet states of *p*-dimethylenequinone is approximately 25 kJ mol^{-1}, so that *p*-dimethylenequinones can exist in the singlet state only at low temperatures, which is consistent with experimental data.[11] On the other hand, calculations have shown[9] that *p*-benzoquinone exists virtually in the singlet state and the probability of its transition to the triplet state is lower by a factor of 2.7 x 10^5 than for *p*-dimethylenequinone.

p-Methylenequinone occupies an intermediate position. The probability of its singlet–triplet transition is only 47 times lower than for *p*-dimethylenequinone and the difference between the energies of the singlet (quinonoid) and triplet (benzenoid) states is about 34 kJ mol^{-1}.[9] Thus the possibility of the conversion of *p*-methylenequinone into a biradical of the hydroxybenzyl type in the absence of factors stabilising the quinonoid bond system is fairly high. This in fact explains why the simplest (unsubstituted) methylenequinone does not exist under the usual conditions and polymerises during its preparation.[12-14]

The stability of methylenequinones increases significantly when one of the reaction centres, for example the oxygen atom, is sterically shielded. Naturally, this effect is manifested to the maximum extent for 2,6-di-t-butylmethylenequinone (I), which dimerises (at a concentration of 0.01 M) 10^3 times more slowly than 2,6-dimethylmethylenequinone (II).[15] The methylenequinone(I) can be isolated in a pure state, although at room temperature it undergoes an irreversible singlet–triplet transition in the course of several minutes with the subsequent formation of characteristic triplet methylenequinone conversion products.[16] The EPR spectrum of the compound in thetriplet state, measured at a concentration of 0.25 M, consists of three triplets and corresponds to the structure of the biradical (III):[17]



(I) (II) (III)

R = t-butyl group

The high degree of stabilisation of the quinonoid bond system of the methylenequinone is obtained as a result of the increase in the conjugation chain of the molecule. This effect is significant for

α-substituted (at the methylene unit) methylenequinones. Thus αα-dicyano-[18] and αα-diphenylmethylenequinones[19] can also be isolated in a pure state; they are less reactive than the methylenequinone (I).

Theoretically, on the basis of the calculation of the electron density and the bond order in the molecule of the simplest methylenequinone by the LCMO method, one may expect three $\pi-\pi^*$ transitions.[20] The most intense ($\lg\varepsilon = 4.05$) long-wavelength transition, corresponding to the wavelength $\lambda_{max} = 287$ nm ($\lambda_{max} = 282$ nm has been found experimentally), is associated with polarisation in the direction parallel to the symmetry axis of the methylenequinone molecule. Two other transitions, with $\lambda_{max} = 274$ nm and $\lambda_{max} = 229$ nm, associated with the polarisation of the molecule in the direction at right angles to the longitudinal symmetry axis, should have a low intensity. They have not been confirmed experimentally.[21] The difference between the λ_{max} of the substituted methylenequinones and the unsubstituted methylenequinone depends on the number and nature of the substituents and is an additive quantity. For any substituted methylenequinones, one can therefore calculate the maximum for the allowed $\pi-\pi^*$ transition from the positions and number of the substituents in the methylenequinone molecule. The wavelength of the main absorption maximum of the substituted methylenequinone is equal to the sum of the wavelengths of the main absorption maximum of the unsubstituted methylenequinone ($\lambda_{max} = 282$ nm) and the increments $\Delta\lambda$ characteristic of the substituents.[22] As can be seen from the data in Table 1, the α-substituents in the methylene unit of the methylenequinone molecule induce a much greater bathochromic shift than the ortho-substituents in the six-membered ring. Such additivity is in fact characteristic of methylenequinones, while in substituted benzoquinones the dependence of the bathochromic shift on the number and nature of the substituents is non-linear.[23].

Table 1. The increments due to the substituents for the calculation of the principal absorption maxima in the spectra of substituted methylenequinones.[8,22]

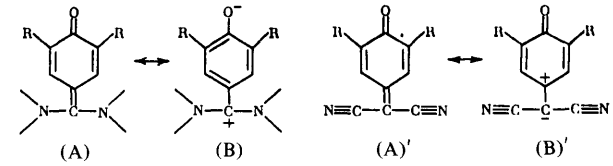


Substituent	Position	Δλ, nm	Substituent	Position	Δλ, nm
CH_3	2(6)	4	$HOCH_2CH=$	4	16
$(CH_3)_3C$	2(6)	4	$HOCOCH=$	4	20*
Br	2(6)	12	$C_6H_5CH=$	4	62*
CH_3O	2(6)	15	$(NC)_2CH=$	4	53
$CH_3CH=$	4	18*	$C_2H_5(CN)CH=$	4	41
$CH_3CH_2CH=$	4	18			
$(CH_3)_2C=$	4	36		4	137*
$CH_3OCH=$	4	40*			
$(CH_3)_2NCH=$	4	95*		4	67*
NCCH=	4	28			
				4	90*

*From Ershov et al.[8]

Semiquantitative data on the π-electron delocalisation in the ground state have been obtained in a study of the ^{13}C NMR spectra of methylenequinones.[24,25] Analysis of the ^{13}C chemical shifts in the six-membered ring and in the methylene group of αα-disubstituted 2,6-di-t-butylmethylenequinones and 2,6-dialkyl-αα-diphenylmethylenequinones showed that the effect of the *ortho*-substituents arises predominantly (to the extent of approximately 80%) via the inductive mechanism, while the influence of α-substituents is associated mainly with conjugation (63–79%).

Depending on the electronegativity of the α-substituents, the carbonyl group of the methylenequinone can function both as an electron acceptor and an electron donor, which is reflected in the two diametrically opposed limiting structures (B) and (B)′, for example, of the molecules of αα-diamino- and αα-dicyano-2,6-di-t-butylmethylenequinones, in which the extent of intramolecular interaction is a maximum:[24]



(A) (B) (A)′ (B)′

On the other hand, in most of the other known methylenequinones the electron distribution obeys the rules for weak charge-transfer complexes, the energy transfer as a result of the intramolecular interaction is proportional to an ionisation potential function of the donor component molecule: $h\nu_i = \gamma I_d - \delta$, where ν_i is the absorption frequency for the ith bond, I_d the ionisation potential of the donor component of the methylenequinone molecule, and γ and δ are constants characterising the acceptor component of the methylenequinone molecule. The γ and δ constants are invariant for a series of αα-disubstituted 2,6-di-t-butylmethylenequinones (the correlation coefficient is $r = 0.967$).[24]

Measurement of the dipole moments of substituted methylenequinone in both ground (μ) and excited singlet (μ*) states confirmed the lability of the conjugated bond system in methylenequinone, which can be expressed by the corresponding contribution of the dipolar structure of type (B). In the ground state, this contribution is 9–18% and depends on the steric effects of the *ortho*-substituents, while in the first excited singlet state it increases to 25–40% and depends less on the character of the *ortho*-substituents in the methylenequinone molecule.[26]

The quantity $\Delta\mu = \mu^* - \mu$, characterising the degree of delocalisation of π electrons, has been found from the calculation and experimental data referring to the variation of the absorption maximum for a series of 2,6-dialkyl-αα-diphenylmethylenequinone in various solvents. The introduction of substituents into the methylene ring increases the dipole moment μ, whose value is correlated with the electrophilic substituent constants σ_p^+, including the inductive and conjugation effects:[27]

$$\mu = [(-7.55 \pm 1.2)\,\sigma_p^+ + 10.94] \cdot 10^{-30}\ (r = 0.993,\ n = 6)$$

The vibrational spectra of methylenequinones are close to those of quinones and quinolide compounds.[28,29] The IR spectra of methylenequinones contain the vibration frequencies of the conjugated carbonyl group, the latter being manifested as a rule by a doublet, and the intensity and positions of the frequencies in the spectrum depend on the nature of the α-substituents.[30,31]

The application of model computational and experimental research methods makes it possible to interpret from a quantitative standpoint the IR spectra of various 2,6-dialkyl-αα-diphenylmethylenequinones and α-substituted 2,6-di-t-butylmethylenequinones.[32,33] It was found that the frequency ν_{CO} can be used to analyse the electronic interactions and the reactivities of the methylenequinones containing various substituents. The frequency ν_{CO} in the IR spectra of methylenequinones is correlated with the electrophilic constants of the substituents:

$$\Delta\bar{\nu}_{CO} = 9.41\ (\pm 0.58)\,\sigma_p^+ + 3.20\ (r = 0.973)$$

and the electronic effects therefore exert a decisive influence on ν_{CO} in methylenequinones. Furthermore, a two-parameter correlation, based on the inductive (σ_I) and the resonance components of the σ constant, has been established, which indicates approximately equal

contributions of the inductive and conjugation effects to the mechanism of the intramolecular interaction via the system of conjugated double bonds in the ground state of methylenequinones:

$$\Delta\bar{\nu}_{CO} = 9.47\,(\pm 2.03)\,\sigma_I + 9.50\,(\pm 0.79)\,\sigma_R^+ + 3.02\ .$$

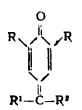
The experimental results were confirmed by a calculation taking into account the dependence of $\bar{\nu}_{CO}$ on the solvent polarity (Table 2). By analysing the vibration frequencies of the carbonyl group and the integral intensities for a series of αα-diphenylmethylenequinones, the contribution of the steric effects to the mobilities of the electrons has been calculated for 2-monoalkyl- and 2,6-dialkylmethylenequinones:[33]

$$\bar{\nu}_{CO} = 35.6\Sigma\sigma_I - 9.1\Sigma\omega + 1625.5\,(r = 0.982)\,,$$

$$A_{CO}^{1/2} = -33.2\Sigma\sigma_I - 128.1\Sigma\omega + 141.1\,(r = 0.942)\,,$$

where ω is a quantity proportional to the van der Waals radii of the substituent and $A_{(CO)}$ is a quantity proportional to the integral intensity of the vibration frequency of the carbonyl group.

Table 2. The experimental and calculated vibration frequencies of the carbonyl group in α-substituted 2,6-di-t-butylmethylenequinones.[30,32]

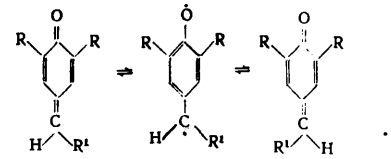


R^1	R^2	ν_{CO}, cm^{-1}	
		calculation	experiment
H	H	1621.7	1615*
H	OCH_3	1614.4	1616
H	CH_3	—	1618
H	C_6H_5	1619.5	1618, 1621*
H	CN	—	1635, 1632*
H		—	1610
CH_3	CH_3	—	1616.5
CH_3	CN	1625.0	—
	CN	—	1635
		—	1592

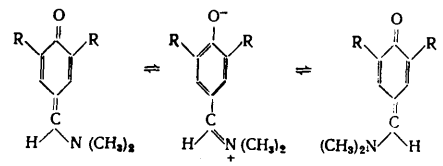
*From Volod'kin and Ershov.[30]

The vibration frequencies of the carbonyl group and the integral intensities diminish with increase in the van der Waals radii of the *ortho*-substituents, the delocalisation of the electrons due to the "*ortho*-effect" in 2,6-dialkylmethylenequinones being approximately 30% higher than in the 2-mono-substituted methylenequinones.

The specificity of the structure and properties of methylenequinones are also manifested in the ^{1}H NMR spectra of these compounds, in the first place as a consequence of the effect due to the hindered rotation about the exocyclic C=C bond.[34,35] This effect was observed for the first time in the analysis of the ^{1}H NMR spectra of substituted stilbenequinones[36] in which the non-equivalence of the *meta*-protons and the protons of the *ortho*-substituents is manifested. The non-equivalence of the ring protons of methylenequinones is associated with the different substituents in the α-position. At room temperature rotation around the exocyclic C=C bond is not observed. The study of the temperature dependence of the ^{1}H NMR spectra of α-substituted methylenequinones showed that the barrier to the intramolecular rotation about the C=C bond in such compounds is fairly high and the activation energy for this transition is greater than 105 kJ mole^{-1}. It has been suggested[35] that the rotation about the exocyclic C=C bond can take place via a biradical transition state:



According to the data of Mannchreck and Kolb,[37] the free electron pair of the nitrogen atom in the molecule of 2,6-di-t-butyl-α-dimethylaminomethylenequinone is coplanar with the cyclohexadiene ring. The ^{1}H NMR spectrum of this methylenequinone is temperature dependent as a consequence of the effects considered above, while the calculated low barrier to the intramolecular rotation about the C=C bond (60.7 kJ mol^{-1}) and the high barrier to the rotation about the C–C single bond (52 kJ mol^{-1}) show that the rotation about the C=C bond takes place via a dipolar transition state, which agrees well with the data considered previously:[24]

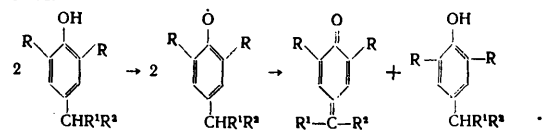


Thus analysis of the physicochemical data on the structure and the influence of substituents on the conjugated system of double bonds in methylene quinones permits a fairly clear-cut formulation of the condition for the stability of methylenequinones (the presence of substituents in the six-membered ring and at the carbon atom of the methylene unit) and makes it possible to deduce the reactivity of these compounds, a characteristic feature of which should be both radical reactions and electrophilic and nucleophilic 1,6-addition reaction by virtue of the presence in the molecule of two reaction centres: the nucleophilic centre at the oxygen atom and the electrophilic centre at the carbon atom of the methylene unit.[38]

III. THE FORMATION OF METHYLENEQUINONES

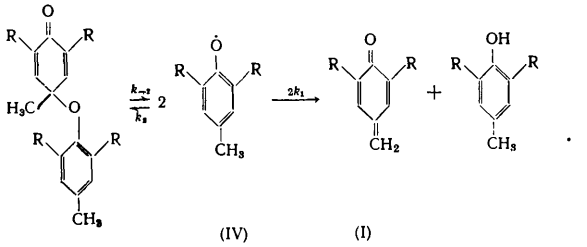
The relation between methylenequinones and phenols is manifested primarily in their interconversions caused by various chemical reagents and the methods of synthesis of stable methylenequinones are therefore mainly based on the reactions of substituted phenols.

The commonest method of synthesis of methylenequinones consists in the oxidation of phenols by variable-valence metal compounds (one-electron oxidation).[39-44] In the presence of α-hydrogen atoms in the molecule of the initial phenol, the phenoxy-radical formed initially disproportionates into methylenequinone and the initial phenol:



The kinetics of the decomposition of the majority of α-hydrogen-containing phenoxy-radicals are bimolecular. However, in the case of the 2,6-di-t-butyl-4-methylphenoxy radical (IV), the kinetics proved to be more complex, which has been the subject of many years' discussion concerning the mechanism of its decomposition. According to the initial view, the phenoxy-radical (IV) isomerises via a first-order reaction to a radical of the hydroxybenzyl type, whose recombination leads to the formation of dimeric compounds.[45-58] However, more recent data[49] confirm that the decomposition mechanism of the radical (IV) via the disproportionation reaction is general and it was found that the order of this reaction depends on the

concentration of the radical (IV). Such dependence is associated with the dimerisation reaction of the radical (IV) which takes place as a parallel process, which is reflected in the relation between the order of the reaction and the concentration of this radical:[50]

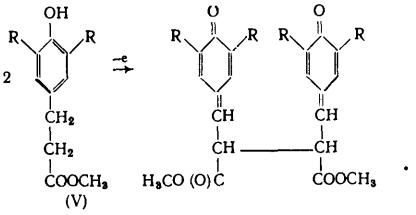


(IV) (I)

It was shown that, when $4K_2[PhO^{\cdot}] \gg 1$, where $K_2 = k_2/k_{-2}$, the decomposition of PhO$^{\cdot}$ is described by a first order law with $k_{eff} = k_1/2k_{-2}$, and, when $4K_2[PhO^{\cdot}] \ll 1$, the decomposition of PhO$^{\cdot}$ is a second order process with $k_{eff} = 2k_1$.

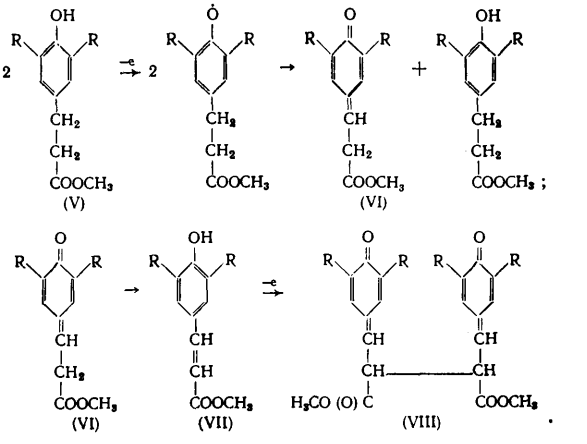
The duration and temperature of the oxidation of the initial substituted phenols are important factors influencing the attainment of the maximum yield of methylenequinones, which is usually associated with the high reactivity of the methylenequinones themselves and their involvement in parallel reactions. Thus the methylenequinone (I) is formed on oxidation of 2,6-di-t-butyl-4-methylphenol (concentration 0.15 M) after 10–15 min in 97–98% yield.[51] The increase in the duration of oxidation to 3–4 h lowers the yield of the methylenequinone (I) to 50% at the expense of its consumption via the spontaneous disproportionation reaction.

The processes in the oxidation of phenols containing hydrogen atoms in the β-position of the carbon chain can vary. For example, whereas the oxidation of 2,6-di-t-butyl-4-(β-phenylethyl)phenol results in the formation of only the corresponding methylenequinone,[52] oxidative dimerisation is observed in the oxidaion of β-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid:[53,54]



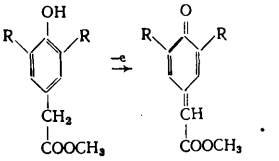
(V)

The study of the mechanism of the oxidation of methyl β-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (V) showed that the methylenequinone (VI) formed in this case is unstable and isomerises spontaneously to the corresponding vinylphenol (VII), whose subsequent oxidation yields the oxidative dimerisation product (VIII). The overall mechanism of the oxidation of the ester (V) by one-electron oxidants can therefore be represented as follows:[55]

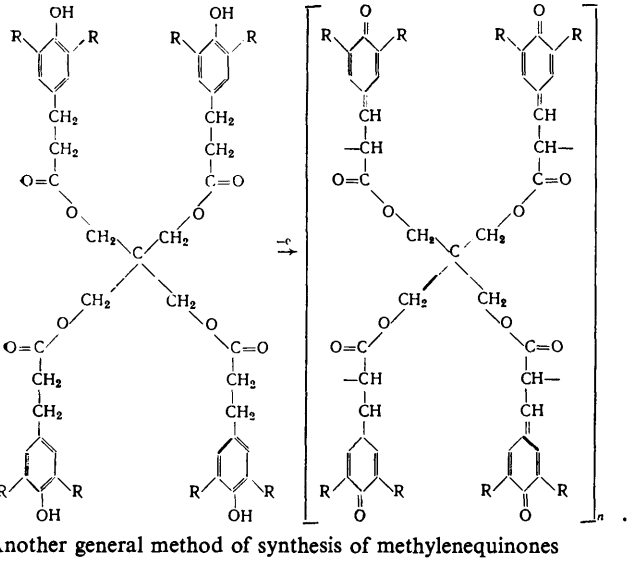


(V) (VI) (VI) (VII) (VIII)

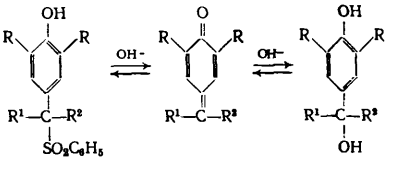
It is noteworthy that, in the oxidation of methyl (3,5-di-t-butyl-4-hydroxyphenyl)acetate, which contains no mobile β-hydrogen atoms, the stable 2,6-di-t-butyl-α-methoxycarbonyl methylenequinone is formed:[51]



Analogous reactions take place also with certain industrial phenolic antioxidants containing several fragments of a sterically hindered phenol in the molecule, for example in the oxidation of the pentaerythrityl ester of β-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid.[7] It was shown kinetically that in this case the destruction of the phenoxy-radicals takes place as a result of the intramolecular reactions of a biradical.[50,56]



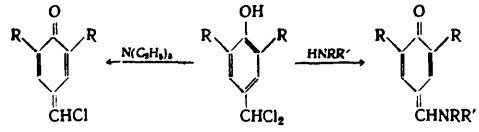
Another general method of synthesis of methylenequinones involves treatment with bases of phenols containing in the benzyl position halogen atoms,[57] the sulpho-group,[58-61] or the hydroxy-group.[62-64] This reaction can be regarded as a special case of the solvolysis of the phenol derivatives indicated, which terminates with the formation of a methylenequinone.[58,59] For example, the methylenequinone (I) is obtained in the reaction of 3,5-di-t-butyl-4-hydroxybenzyl halide with a trialkylamine.[52,56,65] In the general case, the solvolytic reaction in the presence of alkali is reversible and the reactivity of the initial phenols depends on their ability to form a methylenequinone, while the equilibrium constants are determined by the nature of the substituents in the benzyl position:[58,59]



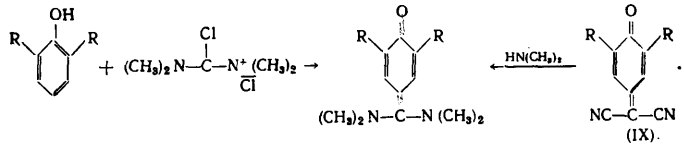
Consequently the yield of the methylenequinone is related to the equilibrium conditions in two reactions.[59]

The interaction of equimolar amounts of di-t-butyl-4-hydroxybenzyl halides with secondary amines also involves the intermediate formation of the corresponding methylenequinones, which are capable of reacting with an excess of the amine to form 3,5-di-t-butyl-4-hydroxybenzylamines.[66,67] However, the reactions of 3,5-di-t-butyl-4-hydroxybenzylidene dichloride with secondary amines terminate

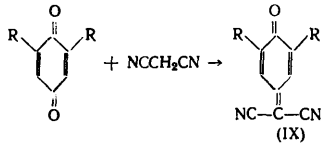
with the formation of 2,6-di-t-butyl-α-(*NN*-dialkylamino)methylenequinones; the above reaction with a tertiary amine yielded 2,6-di-t-butyl-α-chloromethylenequinone:[57]



A number of specific reactions leading to the formation of 2,6-di-t-butyl-α-(*NN*-dialkylamino)methylenequinones are known; for example, the condensation of 2,6-di-t-butylphenol with bis(dimethylamino)methyl chloride[68] and the aminolysis of 2,6-di-t-butyl-αα-dicyanomethylenequinone:[68,69]

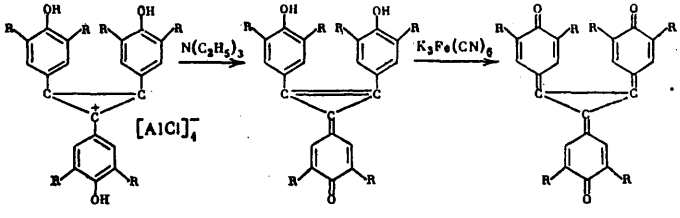


The methylenequinone (IX) has been obtained by condensing 2,6-di-t-butylquinone with malonodinitrile:[69,70]



The interaction of dichlorodiphenylmethane with 2,6-di-t-butylphenol leads to the formation of 2,6-di-t-butyl-αα-diphenylmethylenequinone.[71] Examples of the formation of αα-diphenylmethylenequinones in photochemical reactions have also been described.[72-75]

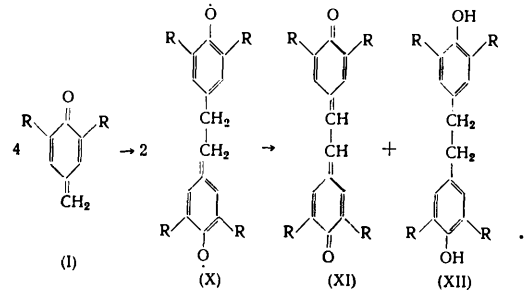
Compounds with a cross-conjugated bond system, which include several structural methylenequinone fragments, constitute a specific group. A general method of synthesis of polymethylenequinones is based on the condensation of 2,6-disubstituted phenols with derivatives of unsaturated cyclic hydrocarbons.[76-87] The complex of tetrachlorocyclopropene with aluminium chloride,[81,83,84,86] the complex of cycloheptatriene with fluoroboric acid,[78,80] and other cyclic unsaturated compounds[82,85] have found wide-scale applications for such purposes. For example, the condensation of 2,6-di-t-butylphenol with tetrachloropropene in the presence of aluminium chloride results in the formation of an adduct with three phenyl molecules, from which a derivative of methylenequinone containing also the aromatic rings of phenol is formed on treatment with a tertiary amine. On treatment with one-electron oxidants, the aromatic rings in such compounds are converted into the cyclohexadiene system with formation of a cross-conjugated bond system:[81]



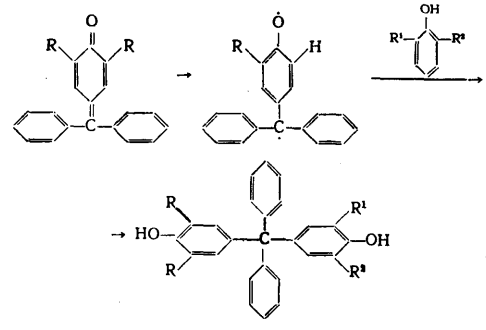
Compounds with such a bond system are relatively stable and can be isolated in a pure state. However, cross-conjugated methylenequinones exhibit very marked oxidising properties and some of them are capable of forming stable radical-anions.[83,84,86,87]

IV. RADICAL REACTIONS OF METHYLENEQUINONES

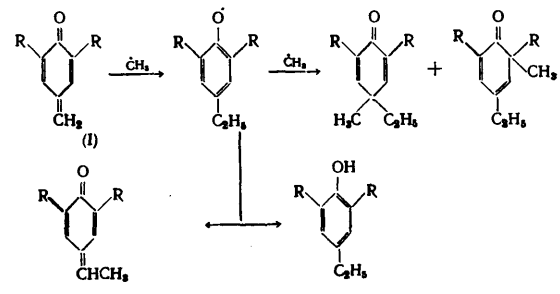
The radical reactions proper of methylenequinones in the form of biradicals (in the triplet state) are characteristic only of the simplest unsubstituted methylenequinones (polymerisation) and the methylenequinone (I), which dimerises spontaneously even in dilute solution with formation of the bisphenoxy-radical (X): Further reactions of this radical lead to a mixture of the stilbenequinone (XI) and dihydroxydiphenylethane (XII):[49,51,56,89]



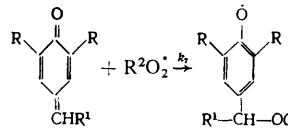
The formation of radical species in the disporportionation of the methylenequinone (I) has been confirmed by EPR.[17] For the stable αα-disubstituted methylenequinones, the singlet–triplet transition can be achieved only in photosensitised reactions. Thus, in the presence of excited benzophenone, 2,6-dialkyl-αα-diarylmethylenequinones react with 2,6-dialkylphenols via a radical mechanism with formation of di(hydroxyaryl)diphenylmethanes:[19]



Apart from the reactions indicated, many methylenequinones are capable of interacting directly with various radicals or of dehydrogenating organic compounds via a radical mechanism. Methylenequinones interact vigorously with alkyl radicals. In the model reaction of the methylenequinone (I) with methylradicals under the conditions of their constant generation as a result of the decomposition of t-butyl hydroperoxide by bivalent iron salts, the radical adds to the carbon atom of the methylene unit of the methylenequinone with formation of an intermediate phenoxy-radical, which is subsequently consumed, fully in conformity with the rules governing the behaviour of phenoxy-radicals, via a disproportionation reaction and via recombination with the methyl radicals present in excess:[56]



The possibility of using methylenequinones in the inhibited oxidation of organic substrates is based on their ability to participate in radical reactions. It follows from kinetic data for the inhibited oxidation of cumene or styrene that methylenequinones react fairly rapidly with peroxy-radicals $RO_2^{\cdot}$:[90]

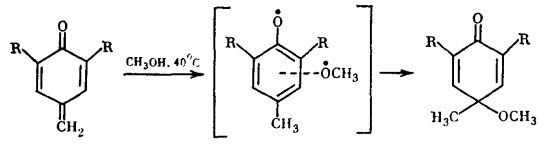


Quantitative estimation of the inhibiting effect of methylenequinones established that the quantity k_7 is independent of the concentration of the methylenequinone and that the phenoxy-radicals formed in this case do not therefore participate in propagating the oxidation chin. Comparison of the values of k_7 for methylenequinones and structurally similar phenols shows that the methylenequinones are somewhat less effective than the phenols in the reaction with phenoxy-radicals (Table 3). However, in this connection attention should be drawn to an interesting fact: the effectiveness of the bismethylenequinone (VIII)—the product of the oxidative dimerisation with the phenolic stabiliser (V)—is approximately equivalent to the effectiveness of the phenol (V) itself. Methylenequinones are effective inhibitors of the radical polymerisation of styrene (concentration 10^{-2} M, initial rate of initiation $w_i = 2.98 \times 10^{-7}$ mol litre^{-1} min^{-1}). The rate constants for the reactions of α-substituted 2,6-di-t-butylmethylenequinones with alkyl radicals are $0.8 \times 10^4 - 1.3 \times 10^5$ litre mol^{-1} s^{-1}, which is higher by 1–2 orders of magnitude than the rate constants for the reactions of the same methylene quinones with alkyl-peroxy-radicals.[91] It follows from the result of the same study that the bismethylenequinone (VIII) is equally reactive in the reactions with both alkyl and alkylperoxy-radicals.

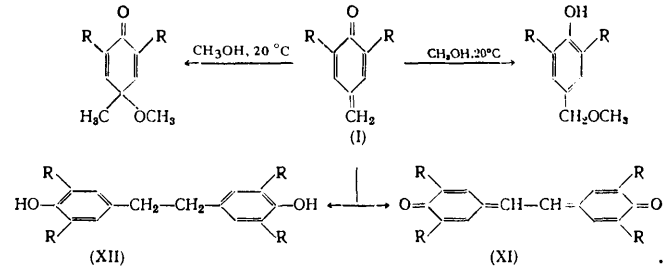
αα-Disubstituted methylenequinones with electronegative substituents do not inhibit the polymerisation of styrene and radical reactions are therefore not characteristic of methylenequinones of this type.

Methylenequinones are also stabilisers of the degradation of high-molecular-weight materials (polymers) and effectively inhibit the oxidation of polyolefins at high temperatures.[7,56] The inhibition of the thermo-oxidative degradation of polymers by methylenequinones is due to their ability to interact with both peroxy- and alkylradicals. This property in methylenequinones is of fundamental importance for the specific synthesis of effective stabilisers in the class of sterically hindered phenols, since the formation of methylenequinones in the primary step of the interaction of the polymeric radical $RO_2^{\cdot}$ with phenolic antioxidants depends on the structure of the sterically hindered phenol and the character of the substituents.

The simplest methylenequinones and the methylenequinone (I) are also capable of dehydrogenating certain organic compounds. For example, the methylenequinone (I) reacts with methanol in dilute solutions at 40 °C to form the methyl ether of the corresponding quinol, the phenoxy-radical produced being directly responsible for the formation of the ether:[51,92]

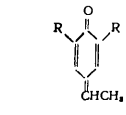
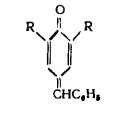
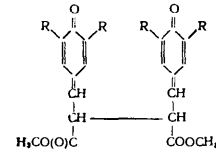
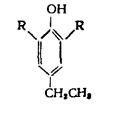
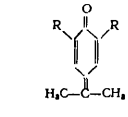
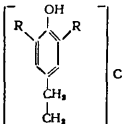


In addition, the formation of 3,5-di-t-butyl-4-hydroxybenzyl methyl ether, possibly via the competing reaction involving the heterolytic 1,6-addition of methanol, is observed. Together with the products of the interaction of the methylenequinone (I) with methanol indicated above, the characteristic products of the reactions of triplet methylenequinone are also formed—the stilbenequinone (XI) and dihydroxydiphenylethane (XII):



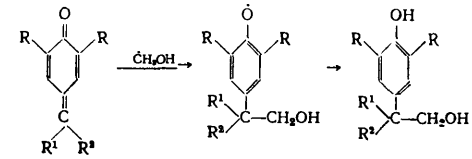
In the presence of catalytic amounts of an acid or alkali, only 3,5-di-t-butyl-4-hydroxybenzyl methyl ether is formed in this reaction.[93]

Table 3. The rate constants for the reactions of methylenequinones and phenols with peroxy-radicals $RO_2^{\cdot}$ in the inhibited oxidation of cumene and styrene.*

Inhibitor	k_7, litre mol^{-1} s^{-1}		Inhibitor	k_7, litre mol^{-1} s^{-1}	
	cumene	styrene		cumene	styrene
	$5.8 \cdot 10^3$	$1.4 \cdot 10^3$		—	$1.8 \cdot 10^2$
	$4.0 \cdot 10^4$	—		$4.0 \cdot 10^4$	$1.0 \cdot 10^3$
	$1.6 \cdot 10^4$	—		$2.9 \cdot 10^4$	—

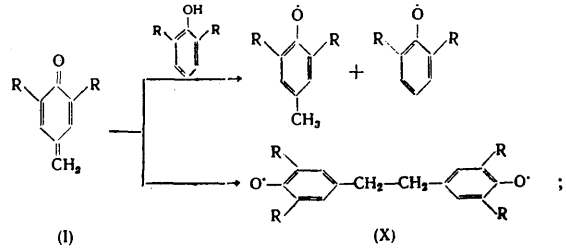
*Determined from the kinetics of the absorption of oxygen in the inhibited oxidation of the hydrocarbons in the presence of an oxidation initiator—azobisisobutyronitrile—at 60 °C.[90]

On irradiation with UV light (mercury lamp), methylenequinones react with methanol somewhat differently. According to the data of Yang et al.[94] and Matsuura and Ogura,[95] when a solution of the methylenequinone (I) or 2,6-di-t-butyl-αα-diphenylmethylenequinone (XIII) in methanol is irradiated, radicals are formed initially from methanol and then react with the methylenquinones. The reaction also proceeds via the phenoxy-radical formation stage:

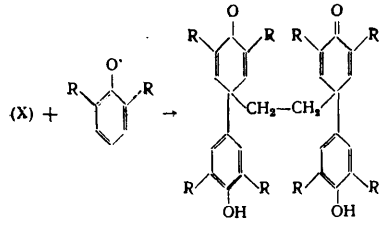


The formation of characteristic radical products has also been noted in the interaction of the methylenequinone (I) in the triplet state with 2,6-di-t-butylphenol[96] and vinylphenols.[97] These are multistage reactions. The phenol is initially dehydrogenated by the

methylenequinone with formation of two phenoxy-radicals, for example, the phenoxy-radical (V) and the 2,6-di-t-butylphenoxy-radical. As noted above, the methylenequinone (I) dimerises spontaneously with formation of the biradical (X), whose recombination with the 2,6-di-t-butylphenoxy-radical leads to the formation of compound (XIV) in 17% yield:[96]

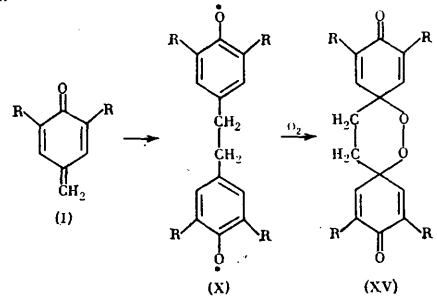


(I) (X)



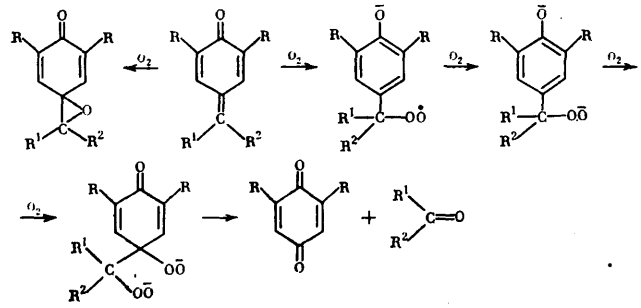
(XIV)

The majority of the known stable methylenequinones are inert in relation to oxygen. However, examples of the catalytic interaction of oxygen with substituted methylenequinones and its non-catalytic reaction with the methylenequinone (I), as a result of which the cyclic peroxide (XV) of the quinolide type is produced, are known. In the given instance, the biradical (X) participates in the reaction with oxygen:[98]



(I) (X) (XV)

In the catalytic oxidation of alkylmethylenequinones, the oxygen adds initially to the methylene carbon, as a result of which a mixture of oxygen-containing compounds is formed: quinols, the corresponding hydroperoxides, and other products.[88,99,100] For example, in the presence of cobalt compound, the reactions considered have a multistage mechanism and the final products are formed as a result of the occurrence of several stages involving the consecutive oxidation and fragmentation of the intermediate relatively unstable radical-ions, dianions of the quinolide type or having an aromatic structure:[101]



The selectivity of this oxidation depends on the nature of the catalyst and the solvent and temperature.

The typical radical reactions examined above are in fact characteristic of the biradical structure of methylenequinones. On the other hand, methylenequinones exhibit the properties of unsaturated carbonyl compounds with their characteristic heterolytic reactions. An example of a reaction characterising the methylenequinone system as a whole is the stepwise electrochemical reduction. The electron, interacting with the substrate, has the properties of both a radical and a nucleophile. As a nucleophile, the electron interacts in the course of the one-electron electrochemical reduction with the overall π-system of the methylenequinone molecule and passes to the lowest unoccupied molecular orbital. The spin density in the radical-anion formed is localised at the methylene carbon atom[102] and the latter therefore possesses the typical properties of radicals of the hydroxybenzyl type with their characteristic dimerisation processes.[51,56] On the other hand, in the initial step of the interaction between the methylenequinone and the electron, the general properties of methylenequinones as unsaturated carbonyl compounds are exhibited and these properties depend to a large extent on the presence and nature of the substituents in the methylenequinone molecule. For this reason, the electrochemical data for methylenequinones will be examined below in the Section devoted to the heterolytic reactions of these compounds.

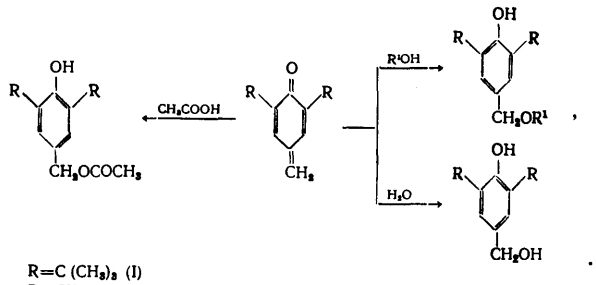
V. HETEROLYTIC 1,6-ADDITION REACTIONS

By virtue of the presence in the conjugated system of atoms with different electronegativities, the methylenequinone molecule contains two reaction centres: a nucleophilic centre which consists of the oxygen of the carbonyl group and an electrophilic centre which consists of the carbon of the methylene unit. Depending on the nature of the attacking agent, the reaction can be directed initially to either of the centres indicated. In both cases the result of the reaction is the same—1,6-addition with formation of phenol derivatives having functional group substituents. Nautrally, the reactions with electrophiles begin with the attack on the most electronegative oxygen atom of the carbonyl group incorporated in the conjugation system of the methylenequinone molecule. 2,6-Disubstituted methylenequinones readily react via the mechanism indicated with many electrophiles, which leads to different phenol derivatives with functional group substituents. Protic acids, water, and alcohols react with alkylmethylenequinones via the same pathway.

In dilute solutions, the methylenequinones (I) and (II) react with alcohols via a pseudofirst-order process and the rate of the latter depends quantitatively on the pK_a of the alcohols.[15,103-105] The hypothesis that associated alcohol species participate in the reaction has been justified kinetically.[105] The methylenequinone (II) is more reactive, its reaction, at a concentration of 10^{-2} M, with methanol being 550 times faster than that of the methylenequinone (I).[15] The rate constant for the reaction of the methylenequinone(II) with t-butyl alcohol (k = 1.2 x 10^{-8} s^{-1}) is smaller almost by three orders of magnitude than in the case of methanol (k = 3 x 10^{-5} s^{-1}) or ethanol (k = 4.5 x 10^{-5} s^{-1}); this methylenequinone reacts with acetic acid at a higher rate (k = 1.35 x 10^{-4} s^{-1}). The dependence of the rate of reaction of the methylenequinone (II) with water on its concentration corresponds to a fractional reaction order, because of the exclusive involvement of associated water species in the reaction.[105]

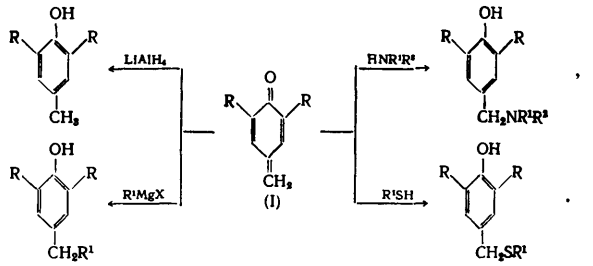
The kinetic features, examined above, of the reactions of 2,6-disubstituted methylenequinones with alcohols, protic acids, and water are valid for dilute solutions at a temperature not higher than 20 °C. Under these conditions, methylenequinones exhibit the properties of unsaturated ketones with their characteristic 1,6-heteroaddition

reactions:

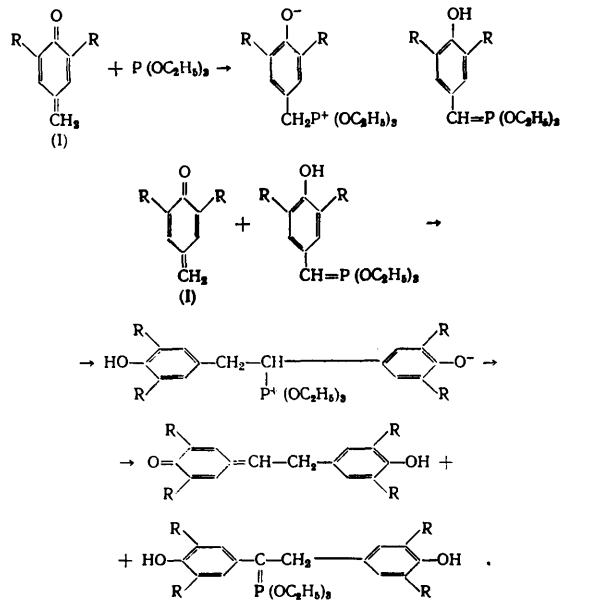


R=C (CH$_3$)$_3$ (I)
R=CH$_3$ (II)

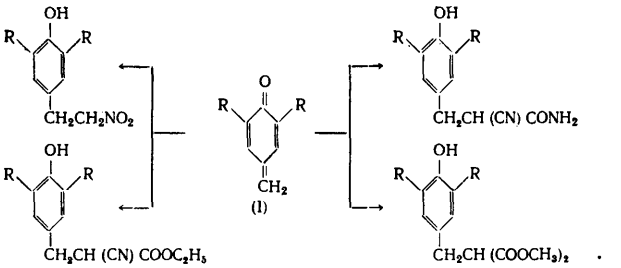
Different workers have investigated most widely the reactions of the methylenequinone (I). which is formed as an intermediate in nucleophilic reactions and on oxidation of a number of derivatives of sterically hindered phenols.[15,30,88,93,106,107] Initially the addition of the nucleophilic species to the methylene carbon atom of the methyl-enequinone molecule also induces the conversion of the quinonoid bond system into an aromatic hydroxy-system and leads to the same reaction product as the initial addition of the proton of the acid reagent. Typical examples of such reactions are those of the methylenequinone (I) with mercaptans, amines, and Grignard reagents, the reduction by alkali metal hydrides, and other reactions:[30,108-112]



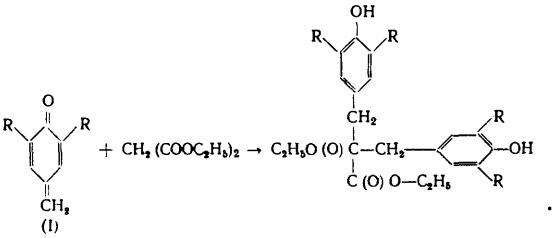
The methylenequinone (I) reacts specifically with triethyl phosphite. This is a multistage reaction:[113]



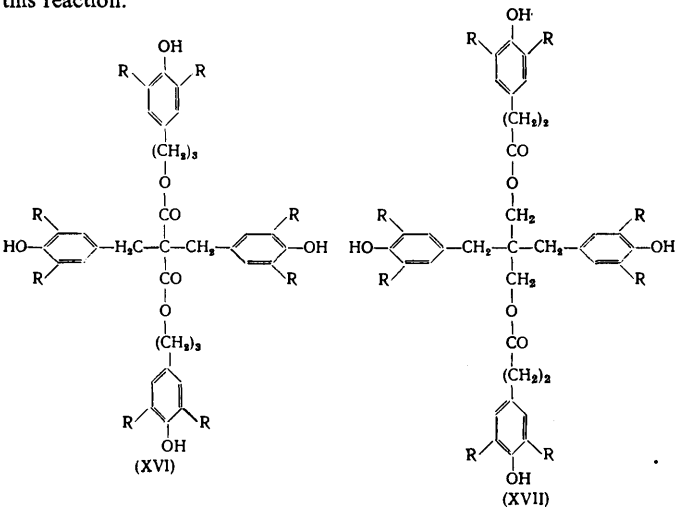
However, as a rule, in most reactions of methylenequinones with nucleophiles a high selectivity is retained, which makes it possible to use them for the synthesis of a wide variety of phenols with functional group substituents, in the first place in the synthesis of antioxidants for the stabilisation of polymers[8,108] and in biological research.[8,114] Thus nitromethane, malonic ester, cyanoacetamide, and cyanoacetic ester add to the methylenequinone(I) with a high degree of selectivity:[115,116]



The nature of the catalyst plays a significant role in the process selectivity. For example, in the presence of potassium t-butoxide, the methylenequinone (I) reacts with malonic ester to form a 1 : 1 adduct, while in the presence of sodium methoxide a 2 : 1 adduct is formed, namely bis(3,5-di-t-butyl-4-hydroxybenzyl)malonic ester:[116,117]



Effective polymer stabilisers (phenozans) have been obtained by this reaction:[117,118]

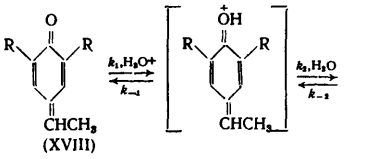


These structurally similar stabilisers are interesting because they behave differently in oxidation by one-electron oxidants. Whereas the oxidation of compound (XVI) leads to the formation of a stable methylenequinone, the oxidation of compound (XVII) involves oxidative dimerisation leading to an increase in the molecular weight of the antioxidant, which significantly improves its thermoprotective properties.[51]

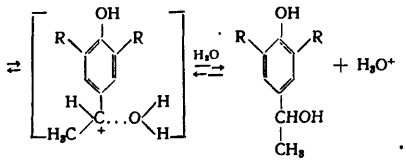
1. α-Alkylmethylenequinones

The homologues of methylenequinones containing alkyl substituents, the carbon atom of the methylene unit and t-butyl groups in the six-membered ring are relatively stable in a pure states. Reactions in the triplet state are no longer characteristic of these

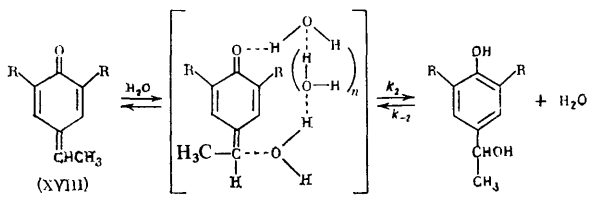
compounds but they retain a high reactivity in reactions with both proton-containing and nucleophilic agents. The effect of the pH of the medium on the mechanism of the 1,6-heteroaddition in reactions of α-alkyl-2,6-di-t-butylmethylenequinones with water is manifested more clearly than in the analogous reaction with the methylenequinone (I) or (II). The following mechanism operates in acid media (pH 2.4 – 5.1):[119]



(XVIII)



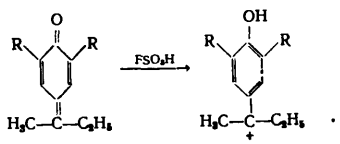
The reaction involving the addition of water to 2.6-di-t-butyl-α-methyl methylenequinone (XVIII) is reversible and the H_2O/D_2O isotope effect is 1.2 in an acid medium. In neutral media (pH 5.1 to 9.5) the transition state incorporates several water molecules and the reaction itself proceeds via the mechanism[119]



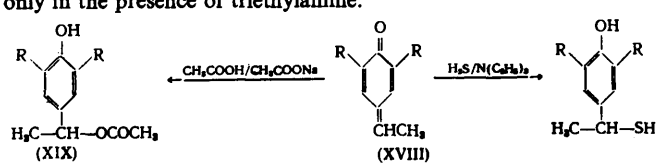
(XVIII)

The H_2O/D_2O isotope effect is 2.56.

The features of the behaviour of the methylenequinone (XVIII) in acid and neutral media examined are general and have been confirmed by other reactions of different α-alkyl- and αα-dialkyl-2,6-t-butylmethylenequinones with alcohols[120] and organic and inorganic acids.[121-124] The formation of the corresponding carbonium ion has been demonstrated by ^1H NMR in the reaction of 2,6-di-t-butyl-α-ethyl-α-methylmethylenequinone with fluorosulphonic acid at -40 °C:[125]

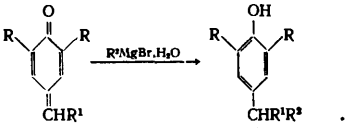


It is noteworthy that the appearance of carbonium ions in the reaction of α-alkylmethylenequinones with proton-containing reagents promotes the irreversible isomerisation of the methylenequinone structure to the aromatic structure of a vinylphenol (see below). The selectivity of many reactions with participation of α-alkylmethylenequinones therefore depends on the specific conditions and increases sharply with increase in the nucleophilicity of the reagent. For example, in the reaction of the methylenequinone (XVIII) with acetic acid, the corresponding 1,6-adduct—3,5-di-t-butyl-4-hydroxy-α-methyl benzyl acetate (XIX)—was obtained in 35% yield, while in the presence of sodium acetate the same reaction takes place more selectively and the yield of compound (XIX) is 90%. The methylenequinone (XVIII) reacts with hydrogen sulphide only in the presence of triethylamine:[30]



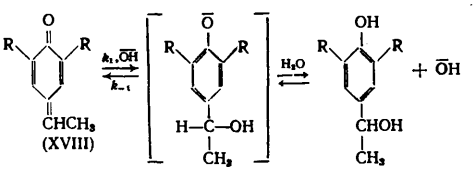
(XIX) (XVIII)

The mode of reaction of methylenequinone homologues with nucleophiles is associated primarily with the characteristic features of the initial step in the interaction of the reagent with the electrophilic centre of the methylene quinone molecule and the character of the decomposition of the intermediate complex formed under these conditions. The reaction of α-alkyl-2,6-t-butyl methylenequinones with amines affords high yields of the corresponding derivatives of *p*-hydroxybenzylamines.[126,127] Organomagnesium compounds also add to the 1,6-positions of the conjugated methylenequinone system with formation of 2,4,6-trialkylphenols; this method has found an application in the synthesis of alkylphenols containing a branched alkyl group in the *para*-position which are difficult to obtain otherwise:[128]



The mechanism of this reaction has not been studied in detail but one can assume that in this instance the addition of the organomagnesium compound takes place synchronously.

In the reaction of the methylenequinone (XVIII) with hydroxide ion (pH 12.3 – 14), 2,6-di-t-butyl-4-vinylphenol is obtained simultaneously with 3,5-di-t-butyl-4-hydroxy-α-methylbenzyl alcohol. The reaction involving the addition of the hydroxide ion to the compound (XVIII) is reversible:[119]



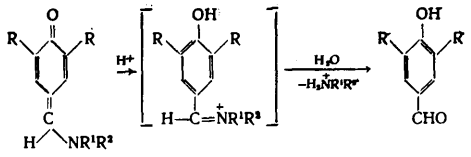
(XVIII)

The rate of the 1,6-addition of water to compound (XVIII) depends on the pH of the medium and is approximately 20 times faster at pH 12.4 – 14 than in neutral media. The reactivity of αα-dialkylmethylenequinones is significantly lower than that of α-alkylmethylenequinones, which is apparently associated with steric factors hindering the attack by the reagent on the electrophilic centre of the methylenequinone molecule.

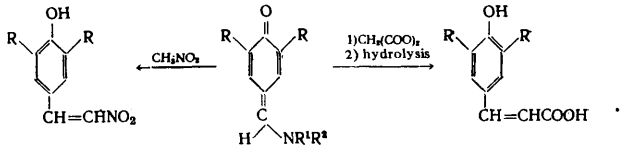
2. Methylenequinones with α-Functional Group Substituents

The electronegative properties of the α-substituent and its capacity to become conjugated with the π-system of the molecule affect directly the reactivity of methylenequinones and this influence is shown most clearly in methylenequinones with α-functional group substituents. Under the influence of the electronic effects of the substituent in the methylene group, the reactivity of the electrophilic and nucleophilic centres of the molecule can alter sharply, which leads in its turn to a change in the behaviour of different α-substituted methylenequinones in the reaction with the same reagent. In the general case in acid media, a proton adding to the carbonyl oxygen atom can induce a bond redistribution with formation of an aromatic system. Naturally, the proton-accepting possibilities of the carbonyl group, which determine the reactivity of methylenequinones in reactions with electrophiles, depend on the degree of conjugation of the π-bond system of the methylenequinone with the α-substituent. αα-(*NN*-dialkylamino)methylenequinones react most readily with acids. The presence of the amino-group in the α-position not only increases the reactivity of the carbonyl group as a result of the high polarisability of the molecule (λ_{max} = 380 nm) but also promotes the aromatisation of the system as a whole by virtue of the possibility of the formation of the azomethine bond system in the transition state. For this reason, αα-(*NN*-dialkylamino)methylene-

quinones are capable of reacting with weak acid reagents, although their reactions in an aqueous medium terminate with the formation of the corresponding *p*-hydroxybenzaldehydes:[30]

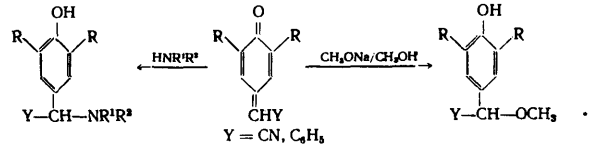


In non-aqueous media, α-(*NN*-dialkylamino)-2,6-di-t-butyl methylenequinones behave as effective *C*-alkylating agents. For example, they react with nitromethane and malonic acid:[30]



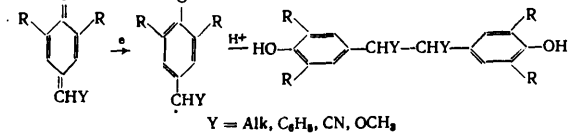
α-Alkoxymethylenequinones behave analogously in the presence of acid reagents. By virtue of the lower nucleophilicity of the oxygen atom at the carbonyl group, α-alkoxymethylenequinones interact only with inorganic or carboxylic acids and do not react with nitromethane, but they do react vigorously with alcohols, amines, and alkalis.[30]

Electron-accepting substituents in the α-position (Y = C_6H_5, COOR, or CN) stabilise the quinonoid bond system of the methylenequinone and the reactions of such methylenequinones with acids beome less typical. However, their reactions with nucleophiles proceed fairly readily with formation of phenolic compounds:[30,69,129]



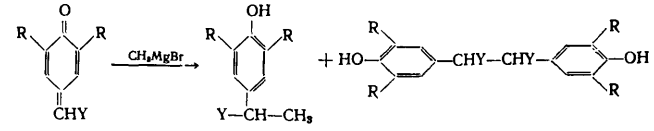
Consequently, in methylenequinones of this kind the carbon atom of the methylene group is fairly reactive with respect to nucleophilic attack.

The most general and typical property of methylenequinones is their ability to participate in oxidation-reduction reactions: a classical example is electrochemical reduction.[108,130,131] The characteristic features of the polarographic reduction of methylenequinones are similar to those of the reduction of quinones. The first polarographic wave of α-substituted 2,6-di-t-butyl methylenequinones in aprotic solvents corresponds to the reversible one-electron reduction, $E'_{1/2}$ depending mainly on the nature of the α-substituent. The main contribution of the electronic effects due to the α-substituent on $E'_{1/2}$ is achieved via the inductive mechanism.[131] The spin density in the radical-anions formed in the one-electron reduction of α-substituted methylenequinones is localised preferentially at the carbon atom of the methylene unit, which determines their ability to undergo spontaneous dimerisation reactions:[102,130]



The dimerisation also occurs under the conditions of the polarographic reduction of α-substituted methylenequinones at a concentration of 10^{-4} M in connection with the high reactivity of the radical-anions produced.

In certain chemical reactions of α-substituted methylenequinones containing electron-accepting substituents, oxidation-reduction processes also take place. For example, the reaction of 2,6-di-t-butyl-α-phenyl- or 2,6-di-t-butyl-α-cyano-methylenequinones with Grignard reagents results in the formation of the corresponding dimers as well as products of the 1,6-addition to the double bond:[56,69]

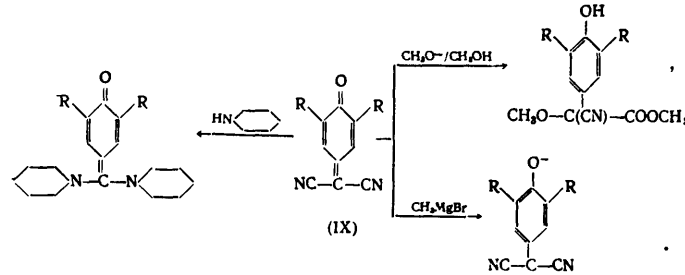


Thus, in the interaction of strong nucleophiles with methylenequinones, a one-electron transfer can take place simultaneously with the main nucleophilic addition reaction.

3. αα-Disubstituted Methylenequinones

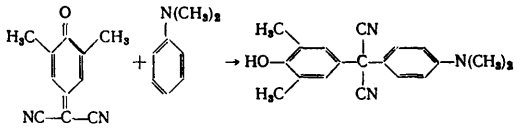
The differences between the properties, chemical behaviour and reactivity of αα-disubstituted methylenequinones containing substituents of different nature are expressed more clearly than for the mono-α-substituted derivatives. In this case, the nature of the functional groups of substituents, their electronegativity, and their capacity for conjugation cause a more marked alteration of the properties characteristic of the unsubstituted methylenequinone and its homologues and new specific properties, characteristic only of the methylenequinones αα-disubstituted by functional groups, appear under these conditions. The fundamental difference in the chemical behaviour of such methylenequinones follows also from the analysis of their physicochemical properties (see above). Thus, on the basis of UV and IR spectroscopic data alone, one can conclude that the "amide" conjugation is so pronounced in αα-(*NN*-dialkylamino)-2,6-di-t-butylmethylenequinones that they virtually lose the properties characteristic of the structure of the mono-α-substituted methylenequinones and that they should be regarded as compounds having a zwitter-ionic structure. These compounds hardly dissolve in organic solvents and are characterised by a high melting point and a high dipole moment (10.8 D).[24]

On the other hand, the quinonoid bond system becomes stable in methylenequinones with electronegative substituents. Such methylenequinones are inert in relation to protic acids and only reactions with nucleophiles become characteristic of them. For example, compound (IX) exhibits very pronounced electron-accepting properties and is capable of forming donor–acceptor complexes with amines and alkoxides. The interaction of the methylenequinone (IX) with a Grignard reagent results in the appearance of a stable radical-anion.[69] The final product of the reaction of the methylenequinone (IX) with piperidine is 2,6-di-t-butyl-αα-dipiperidinomethylenequinone, while its reaction with sodium methoxide leads to the formation of the product of the addition of methanol with partial alcoholysis of one of the nitrile groups:[56]



2,6-Disubstituted αα-dicyanomethylenequinones are stable in acid media, although 1,6-addition reactions are possible under the influence of nucleophiles. In this sense, data concerning the use of

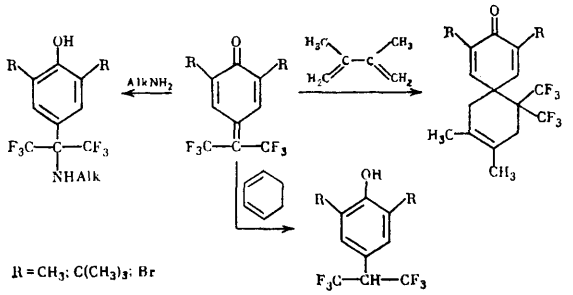
αα-dicyano-2,6-di-methylmethylenequinone as an alkylating agent for dimethylaniline are of definite interest:[18,132]



The majority of αα-disubstituted methylenequinones with electronegative substituents are stable compounds whose stability is almost independent of the presence of substituents in the six-membered ring, which is apparently associated with the sharp decrease of the mobility of the *p*-electrons of the carbonyl group and the consequent loss of capacity for protonation in acid media.

The electron-accepting properties and the electron affinities of αα-diphenylmethylenequinone are almost independent of the character of the substituents in the six-membered ring, their polarographic reduction potentials are similar, and the 1,6-addition reactions take place only under the conditions of base catalysis. For example, the methylenequinone (XIII) does not react with amines and sodium methoxide, but, in the presence of potassium t-butoxide, acetonitrile adds to it.[133,134] 2,6-Dialkyl-αα-diphenylmethylenequinones are capable of forming complexes with phenols and the enthalpy of formation of a hydrogen bond in these complexes increases sharply with decrease in the steric effect generated by the alkyl substituents in the initial methylenequinones.[135]

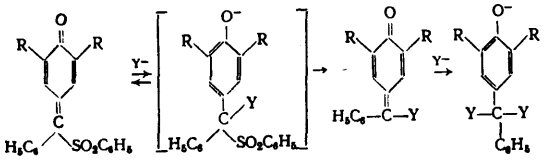
Other examples confirming the similarity of the influence of electronegative α-substituents on the properties of αα-disubstituted methylenequinone are the reactions of 2,6-dialkyl-αα-bis(trifluoromethyl)methylenequinones, which interact with amines and unsaturated compounds but are stable in relation to acids:[136]



R = CH_3; $C(CH_3)_3$; Br

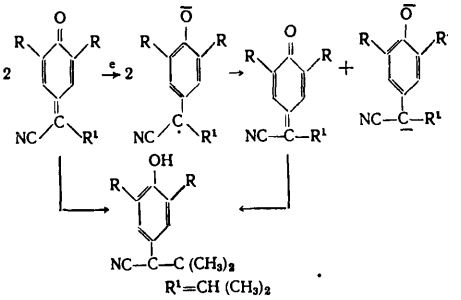
Finally, the reactivity of 2,6-di-t-butyl-α-chloro-α-trifluoromethylmethylenequinone is reduced so much that it has become inert in relation to nucleophiles and is even stable in the presence of alkali metal hydrides.[137]

Reactions leading to the replacement of one of the α-substituents are also characteristic of compounds of the type considered. The characteristic features of the substitution reactions involving αα-disubstituted methylenequinones depend on the thermodynamic stability of the intermediate phenoxide ion and on the strength of the bonds between the α-substituents and the carbon atpm of the methylene unit. An example of such reactions is provided by the substitution of a α-benzenesulphonyl group when 2,6-di-t-butyl-α-phenyl-α-benzenesulphonylmethylenequinone is acted upon by nucleophiles:[138]



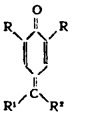
Reactions of this type, involving nucleophilic substitution and subsequent addition, have been investigated under conditions where the above methylenequinone was acted upon by alkalis, alkoxides, thiophenoxides, and cyanides. The method has found an application in the synthesis of derivatives of sterically hindered phenols which are otherwise difficult to obtain.

Quantitative data characterising the influence of α-substituents of different nature on the reactivity of αα-disubstituted 2,6-di-t-butylmethylene quinones in the reaction with the simplest nucleophile (the electron) have been obtained as a result of polarographic measurements and electrochemical studies (Table 4). In this series, the greatest electron affinity is shown by the methylenequinone (IX), whose electrochemical reduction takes place in two stages, a stable radical-anion being formed at the potential of the first polarographic wave $E'_{1/2}$. This method makes it possible to estimate the reactivity of methylenequinones containing in the α-positions simultaneously electron-accepting and electron-donating substituents. Furthermore, it has been possible to establish the characteristic features of the electrochemical reduction of 2,6-di-t-butyl-α-cyano-α-isopropyl methylenequinone associated with the phenomena involving the disproportionation of the intermediate radical-anion and the isomerisation of the initial methylenequinone to vinylphenol under electrochemical reduction conditions:[56]



The EPR spectrum of the radical-anion has been recorded in the course of the reduction of 2,6-di-t-butyl-α-cyano-α-isopropylmethylenequinone by metallic potassium in tetrahydrofuran.[56]

Table 4. The half-wave potentials (relative to the saturated calomel electrode) for the polarographic reduction of αα-disubstituted 2,6-di-t-butyl methylenequinones (in dimethylformamide with tetrabutylammonium perchlorate as the supporting electrolyte).[56]

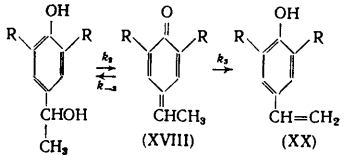


R^1	R^2	$E'_{1/2}$, mV	$E''_{1/2}$, mV	R^1	R^2	$E'_{1/2}$, mV	$E''_{1/2}$, mV
CH_3	CH_3	1370	—	CH_3	CN	750	1480
C_6H_5	C_6H_5	570	1130	C_2H_5	CN	770	1490
CN	CN	120	990	$CH(CH_3)_2$	CN	780	1500
NC_5H_{10}	NC_5H_{10}	2125	2275	C_6H_5	CN	570	1130
C_6H_5	NC_5H_{10}	1516	—	NC_5H_{10}	CN	949	1544

VI. ISOMERISATION OF METHYLENEQUINONES

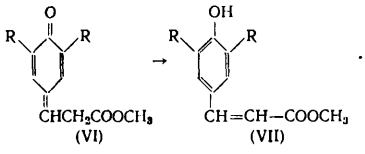
The high reactivity of methylenequinones is associated with thermodynamic factors and the possibility of a rearrangement of the bond system of the methylenequinone to the aromatic bond system of a phenol. This possibility is manifested clearly in the isomerisation of methylenequinone homologues to vinylphenols. The isomerisation of alkylmethylenequinones to vinylphenols is irreversible,

so that many reactions of the methylenequinones are accompanied by the formation of vinylphenol derivatives. Thus in an aqueous medium at pH 8.2 the isomerisation of the methylenequinone (XVIII) to 2,6-di-t-butyl-4-vinylphenol (XX) takes place simultaneously with its hydration, both reactions proceeding at similar rates under the conditions indicated (k_2/k_3 = 2.8):[119]



(XVIII) (XX)

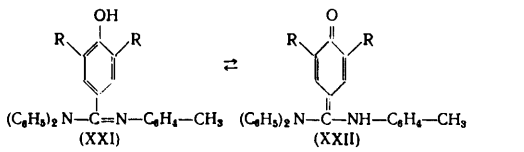
In acid or alkaline media, the rate of the 1,6-addition reaction is significantly higher than the rate of isomerisation, but, with increase in the reaction time, the yield of the phenol (XX) increases because of the irreversibility of the isomerisation stage. At 70–75 °C the irreversible isomerisation of α-alkylmethylenequinones takes place in the presence of alumina.[139] Vinylphenols are obtained in substitution reactions with participation of benzyl derivatives of phenol. Many of these reactions proceed via a stage involving the formation of the corresponding methylenequinones, whose isomerisation actually leads to the vinylphenols.[140,141] The functional-group substituents in the α-position promote the isomerisation of methylenequinone to vinylphenol, the process actually occurring spontaneously at room temperature, for example:[56]



(VI) (VII)

The pure methylenequinone (VI) rearranges quantitatively to a cinnamic acid derivative after two days at 20 °C.

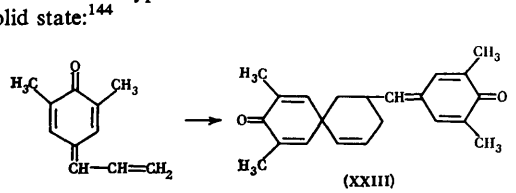
Under the influence of functional-group substituents in the α-position, the thermodynamic stability of the methylenequinone structure increases and tautomeric transformations are observed in the case of α-aminomethylenequinones.[142] For example, the prototropism of 3,5-di-t-butyl-4-hydroxy-*NN*-diphenyl-*N'*-tolybenzamidine (XXI) is observed in solution and leads to the establishment of thermodynamic equilibrium with the corresponding αα-diaminomethylenequinone (XXII):



(XXI) (XXII)

Both tautomers, (XXI) and (XXII), have been isolated in a pure state. At 25 °C, the ratio of compunds (XXI) and (XXII) is 42 : 58, $\Delta G^{\ddagger}_{298}$ = 70.8 kJ mole^{-1}, and $\Delta S^{\ddagger}$ = −16.4 e.u. The solvent polarity affects the ratio of the tautomers in solution and hence the nature of the solvent is one of the factors influencing the stability of the methylenequinone bond system.[143]

Methylenequinones containing vinyl substituents in the α-position undergo Diels-Alder-type dimerisations in concentrated solutions or in the solid state:[144]



(XXIII)

The cyclohexadiene structure is retained in reactions of this type and a methylenequinone (XXIII) derivative having a more complex structure is formed. The dimerisation reaction is irreversible.

—o0o—

The interest in the chemistry of methylenequinones has not weakened for a long time. In our day, they remain convenient objects for the investigation of various aspects of theoretical and synthetic organic chemistry and photochemistry and also for the study of the pathways leading to the biogenesis of natural products.

The structure of methylenequinones is labile, which is the reason for their high reactivity. Both homolytic and heterolytic reactions are characteristic of them. Being vinylogues of ketones, methylenequinones possess also many of their properties, but these are manifested more strikingly and are more varied.

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Carcinogenic *N*-Nitrosamines. Formation, Properties, and Analysis

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Literature data on the formation of carcinogenic *N*-nitrosamines in the environment, their physicochemical properties, their action on the human organism, the methods for their microanalysis, and also their content in the atmosphere, water sources, soil, and industrial agricultural and food products are described systematically and surveyed. The principal features of this comparatively new class of powerful chemical carcinogens are indicated.
The bibliography includes 284 references.

CONTENTS

I. Introduction 350
II. Methods of synthesis of *N*-nitrosamines 350
III. Properties of *N*-nitrosamines 355
IV. Principal methods of microanalysis 357
V. The content of *N*-nitrosamines in objects in the environment 359

I. INTRODUCTION

A distinct tendency towards an increase in the pollution of the environment as a consequence of the intense technological activity by man can be traced during the last decade. A constant increase in the amount of bound nitrogen in the biosphere as a result of the increase in the scale of industrial manufacture, the consumption of fuel, the use of nitrogen-containing fertilisers and pesticides, the ejection into the atmosphere of nitrogen oxides, ammonia, amines, etc. has been noted.

The pollution of various objects by compounds with a high toxicity and carcinogenic and mutagenic properties is especially undesirable. Among substances of this type, the large group of *N*-nitroso-compounds, in which aliphatic and certain cyclic *N*-nitrosamines (NA) exhibit a high carcinogenic activity, can be distinguished. These compounds have been known for more than 100 years but due attention has not been paid to their investigation. Certain NA have been used in industry as solvents, intermediates for the synthesis of substituted hydrazines, etc. In the middle of the 1950's, it was observed that *N*-nitrosodimethylamine induces liver tumours in animals and in subsequent years it was established that about 200 different nitroso-compounds exhibit a carcinogenic activity.[1-5] About 1500 publications annually have been devoted recently to the study of the properties of this comparatively new class of carcinogens and especially of their biological activity.[6]

NA are fairly stable and are capable of circulating for a long time in the environment, which results in the pollution of various objects. It has been established that NA are contained in water, air, soil, food and industrial products, agricultural pesticides and herbicides, medicinal drugs, etc. and that the compounds most often detected are *N*-nitrosodimethylamine (NDMA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosopyrrolidine (NPyr), and *N*-nitrosopiperidine (NPip). *N*-Nitrosodipropylamine (NDPA), *N*-nitrosodibutylamine (NDBA), *N*-nitrosoethylmethylamine (NEMA), *N*-nitrosomorpholine (NMor), *N*-nitrosothiazolidine (NThia), etc. are more rarely encountered.[3-5,7-11]

An important feature of NA compared with other classes of carcinogens is the possibility of their ready formation directly in various objects as a result of nitrosation. Amines and many other nitrogen-containing substances as well as different nitrosating agents are widely distributed in water, air, food products etc.

Data on the biological activity of NA and their presence in objects in the environment have been published in a series of reviews and monographs.[2-4,8,12-20] This review deals with processes leading to the formation of NA, the chemical reactions determining their properties and transformations, and methods for their analysis and surveys data on the content of these compounds in various objects.

II. METHODS OF SYNTHESIS OF *N*-NITROSAMINES

The main process leading to the formation of NA is nitrosation. The compounds nitrosated can be various mono-, di- and polyamines as well as other nitrogen-containing compounds. Secondary and tertiary amines as well as other compounds containing the $(CH_3)_2N$ and $(C_2H_5)_2N$ groups are most readily and rapidly nitrosated. The nitrosating agents are usually nitrous acid derivatives XNO (X = halogen, NO_2, NO_3 OH_2^+, or OR) as well as the nitrosonium cation, etc.[21-25] The nitrite ion and free HNO_2 are converted into active nitrosating agents in an acid medium:[21,23,25-30]

$$2NO_2^- \xrightarrow{H^+} 2HNO_2 \rightleftarrows H_2ONO^+ + NO_2^- \rightleftarrows N_2O_3 + H_2O\,.$$

At low pH, there is a possibility of the formation of the nitrosonium cation:

$$N_2O_3 + 3H_2SO_4 \rightarrow 2NO^+ + 3HSO_4^- + H_3O^+\,.$$

In the presence of nitrogen halides, HNO_2 is capable of giving rise to the corresponding nitrosyl halides;[21,31]

$$HNO_2 + HCl \rightleftarrows NOCl + H_2O\,.$$

Nitrosating agents can be arranged in the following sequence in order of the decrease in their activity: $NO^+ > H_2ONO^+ > NOCl > N_2O_3$.[21,25,32] In aqueous solutions of nitrites and nitrous acid at pH below 5, various nitrosating agents and their mixtures can be present.[21,23,33]

1. Nitrosation of Amines

The nitrosation of secondary amines is usually used for the synthesis of NA and is the main cause of their formation in various objects.[12,21,22,26,29,34] Nitrosation by various agents takes place in water, mixtures of water with organic solvents, in organic solvents, in the gas phase, and also directly in various objects over a wide temperature range.[4,17,22,29,30,33-39] In solutions, this reaction ensures a high yield of NA:[21,22,29,36,40,41]

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!NH + NOY \rightarrow \left[\begin{matrix} R \\ R' \end{matrix}\!\!>\!NHNO\right]^+ Y^- \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!NNO + HY\,.$$

Under certain conditions, secondary amines are capable of being converted into the corresponding NA on treatment with not only active nitrosating substances but even sodium nitrite. In aqueous solutions of $NaNO_2$ and a secondary amine, the following reactions are possible under the influence of sunlight, UV light, or γ-radiation:[42-45]

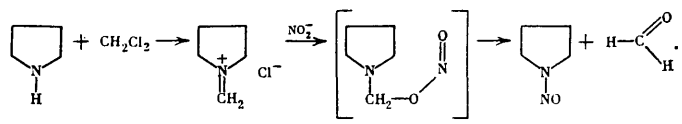
$$2NO_2^- + H_2O \rightarrow N_2O_3 + 2HO^-,$$

$$N_2O_3 + \underset{R'}{\overset{R}{>}}NH \xrightarrow{HO^-} \underset{R'}{\overset{R}{>}}N{-}NO + H_2O + NO_2^-,$$

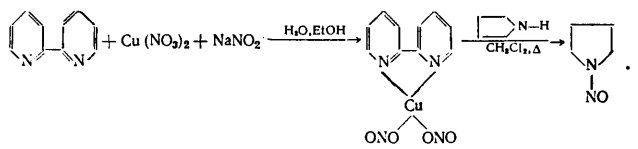
$$2NO_2^- + 2H_2O \rightarrow N_2O_4 + 2HO^- + 2HO^-,$$

$$N_2O_4 + \underset{R'}{\overset{R}{>}}NH \xrightarrow{HO^-} \underset{R'}{\overset{R}{>}}N{-}NO + H_2O + NO_3^-.$$

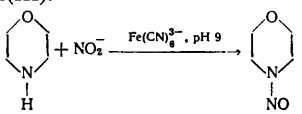
Certain secondary amines are nitrosated in methylene chloride with sodium nitrite,[30,35,46] for example:[35,46,47]



A series of metal salts promote the reaction of secondary amines and nitrites in neutral and basic media.[22,29,47-49] Thus pyrrolidine interacts fairly readily with $NaNO_2$, 2,2′-bipyridyl, and copper nitrate:[49]



Instead of 2,2′-bipyridyl, it is possible to use pyridine although with less success.[49] The reaction of morpholine with $NaNO_2$ is promoted by hexacyanoferrate(III):[21,49]



Secondary amines interact analogously with sodium nitroprusside:[22,50,51]

$$\underset{R'}{\overset{R}{>}}NH + Fe(CN)_5NO^{2-} \xrightarrow{OH^-} \underset{R'}{\overset{R}{>}}NNO.$$

Presumably the promoting action of hexacyanoferrate(III) on the nitrosation reaction is caused by the preliminary formation of the nitroprusside ion. This has been confirmed to some extent by the interaction of hexacyanoferrate(II) with nitrite:[49]

$$Fe(CN)_6^{4-} + NO_2^- \rightarrow Fe(CN)_5NO_2^{4-} + CN^-,$$

$$Fe(CN)_5NO_2^{4-} + 2H^+ \rightarrow Fe(CN)_5NO^{2-} + H_2O.$$

The nitrosation of secondary amines in the presence of certain aldehydes, for example, formaldehyde takes place in an alkaline medium.[4,28,47,52]

The nitrosation of secondary amines by gaseous nitrogen oxide is of practical interest from the standpoint of the formation of NA in various objects. Air usually contains N_2O_3 and N_2O_4 which are capable of interacting with secondary amines dissolved in water or organic solvents and also those present in various objects:[29,36,27,42,53]

$$2\,\underset{R'}{\overset{R}{>}}NH + 2N_2O_4 \rightarrow \underset{R'}{\overset{R}{>}}N{-}NO + \underset{R'}{\overset{R}{>}}N{-}NO_2 + HNO_3 + HNO_2.$$

On treatment with gaseous N_2O_3 nd N_2O_4, NA are formed in aqueous solutions over a wide pH range, even at pH > 5, which can be explained by the high rate of nitrosation of secondary amines compared with hydrolytic reactions.[29,36,42] Analogous results have been obtained in the nitrosation with gaseous nitrosyl chloride.[21,36,42] NA are also formed in air from secondary amines and gaseous nitrogen oxides.[36,37,54-57] It is believed that this reaction is initiated by photodissociation and takes place via a radical mechanism:[36,37,42,56,58]

$$HONO \xrightarrow{h\nu} NO^{\cdot} + HO^{\cdot} \xrightarrow{\underset{R'}{\overset{R}{>}}NH} H_2O + \underset{R'}{\overset{R}{>}}N^{\cdot} \xrightarrow{NO^{\cdot}} \underset{R'}{\overset{R}{>}}N{-}NO.$$

Certain organic compounds containing the NO_2 or ONO groups are also capable of nitrosating secondary amines. Aliphatic polynitro-compounds are known to be capable of acting as "NO_2-producing substances".[32,50] It has been shown that tetranitromethane, 2,2-dinitropropanol, and 2-bromo-2-nitropropane-1,3-diol afford NMor on heating with morpholine.[59] The mechanism of this reaction has been inadequately elucidated.

The nitrosating activity of nitrous acid esters has been more fully investigated:[31,42,60-65]

$$R''{-}ONO + HY \rightarrow \left[R''{-}\underset{H}{\overset{|}{O}}NO\right]^+ Y^- \rightarrow R''{-}OH + Y{-}NO,$$

$$\underset{R'}{\overset{R}{>}}NH + Y{-}NO \rightarrow \underset{R'}{\overset{R}{>}}N{-}NO + HY.$$

On exposure to UV irradiation, this reaction can have a radical mechanism.[12,31,61] The thioesters of nitrous acid react analogously.[60,62,65-68]

The transnitrosation reaction, which is not used for the synthesis of NA but can occur in various objects and in the organism, is of significant interest. Various nitroso-compounds, especially those which have no carcinogenic activity or their carcinogenic activity is weak, can act as nitrosating agents and transnitrosation can result in the formation of active carcinogens.[69-72] A series of nitroso-compounds which are quite effective in this reaction, including heterocyclic and aromatic compounds and substituted ureas and urethanes, have been discovered. As a rule, they are all readily obtained by nitrosating substances containing $\rangle$NH group and have a fairly labile NO group.[69,72,73] The nitrosation reactions with participation of the non-carcinogenic nitrosodiphenylamine (NDPhA), used in the rubber industry, have been studied in fair detail. The conditions for the occurrence of this reaction both in various solutions and in the organism have been discovered and a probable process mechanism has been proposed:[70,71,73]

$$(C_6H_5)_2N{-}NO + HY \rightarrow \left[(C_6H_5)_2N\underset{NO}{\overset{H}{<}}\right]^+ Y^- \rightarrow (C_6H_5)_2NH + Y{-}NO,$$

$$\underset{R'}{\overset{R}{>}}NH + Y{-}NO \rightarrow \underset{R'}{\overset{R}{>}}N{-}NO + HY.$$

The reaction is accelerated in the presence of SCN^- and I^- ions.[70,73] When solutions of NDPhA are heated, the following reactions occur:[21,71]

$$2\,(C_6H_5)_2N{-}NO \xrightarrow{\Delta} (C_6H_5)_2N{-}N(C_6H_5)_2 + 2NO,$$

$$\underset{R'}{\overset{R}{>}}NH + NO \xrightarrow{O_2 \text{ or catalyst}} \underset{R'}{\overset{R}{>}}N{-}NO.$$

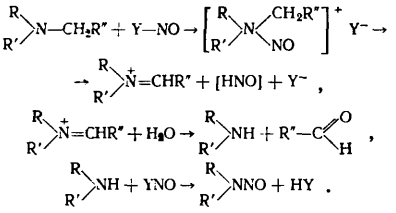
The reaction of NDPhA with dibutylamine results in the formation of NDPA, that with morpholine affords NMor and that with tetramethylthiuran disulphide gives rise to NDMA.[71] Mono- and di-isonitrosopiperazines are also effective in transnitrosation reactions.[41,73]

Transnitrosation with nitrosoaminoacids, which are readily formed in various objects and in the organism, has been investigated.[70-73] Thus the interaction of nitrosoproline or hydroxynitrosoproline with morpholine in animal organisms has led to the detection of NMor.[69]

The possibility of nitrosating secondary amines by nitrates after the conversion of the latter into NO_2^-, NO_2, or NO is of practical interest. The microbiological and chemical reduction of nitrates occurs widely both in objects in the environment and in the organism.[7,13,18,33,34,42,45,47,74,75] The presence of high concentrations of nitrates in the soil, in water, in mineral fertilisers, in food products, in various types of animal feed, etc. makes a significant contribution to the pollution of various objects by nitrosamines.

Numerous studies have demonstrated that NA are formed from secondary amines and various nitrosating agents directly in human and animal organisms.[8,12,17,18,53,76-82]

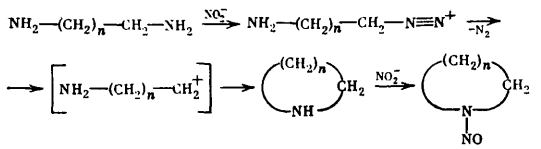
The nitrosation of various tertiary amines, which takes place in a complex manner, has been fairly widely investigated. The majority of workers believe that the nitrosation is preceded by a cleavage stage:[27,34,41,63,83,87]



This mechanism has been demonstrated by isolating the reaction mixture and identifying the NA, the corresponding aldehyde, and the [HNO] conversion product—nitrous oxide.[41,84] Tertiary amines are nitrosated with more difficulty than secondary amines; even under optimum conditions, the yield of NA is significantly lower and rarely reaches 40–50%.[32,41,83,84,87,88] However, it has been noted that trimethylamine and also trimethylamine oxide form NDMA fairly rapidly.[27,41,84,89,90] The ease of nitrosation of tertiary amines decreases appreciably with increase in the number of carbon atoms in the amine.[21,41,84,87,89,90] As a rule, a series of side products are formed together with the NA under severe conditions.[41,83,87,88] The formation of NA from tertiary amines has been demonstrated in various objects and also directly in the organism.[13,34,41,76,84,89,90]

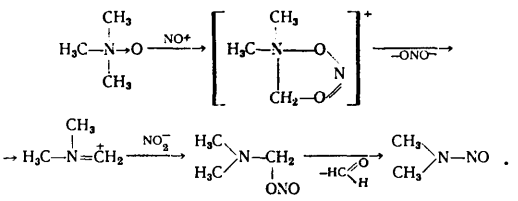
The interaction of nitrosating agents with primary amines has been less thoroughly investigated. These reactions proceed via various fairly complex mechanisms and the yield of the NA is in most cases insignificant.[12,21,32,91,92]

Certain primary di- and poly-amines, including biologically active compounds such as putrescine, cadaverine, spermine, and spermidine can give rise to cyclic NA on nitrosation:[4,5,91,93]



Putrescine reactions with nitrous acid to produce NPyr in yields up to 1.6%.[92-94] For comparison, we may note that the yield of NDBA in the nitrosation of n-butylamine under the same conditions is only 0.01%.[92,94] The nitrosation of primary amines in various objects and in the organism is possible, but this gives rise to only small amounts of NA.[4,91-93]

The nitrosation of quaternary ammonium compounds takes place at elevated temperatures and high concentrations of the starting materials, the yield of the NA being insignificant.[95-97] The mechanism of these processes has been inadequately investigated. It is assumed that tetramethylammonium salts are less capable of being nitrosated than dimethylamine oxide:[84,85,95,97]

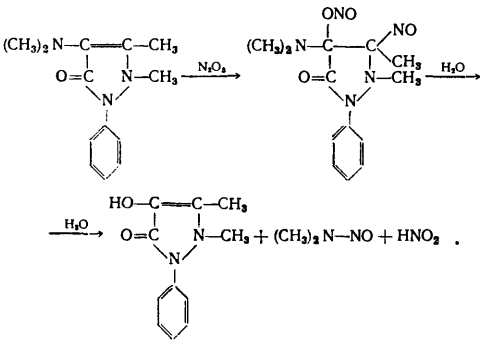


Tetra-alkylammonium compounds can be nitrosated in heterogeneous media on treatment with gaseous nitrogen oxides.[89,90] This reaction leads to pollution with nitrosamines of the products in which high concentrations of trimethylamine, acetylcholine chloride, choline chloride, etc. have been detected.[84,89,90,96,97]

2. Nitrosation of Other Nitrogen-containing Substances

The nitrosation of a series of nitrogen-containing substances with formation of NA can occur in two ways: the insertion of the NO-group in the molecule and the formation of complex nitroso-compounds or the cleavage of the nitrogen-carbon bonds and the interaction of the amino-groups with nitrosating agents. Reactions of the first type have been described in a number of studies.[4,12,27,95,98,99] We shall consider processes which result in the formation of volatile NA—the "nitrosative deamination" reactions.[21,24,100-102]

Certain nitrogen-containing substances are capable of reacting with nitrosating agents at unexpectedly high rates. Thus aminopyrine (2,3-dimethyl-4-dimethylamino-1-phenyl-3-pyrazolin-5-one) is rapidly nitrosated in homogeneous and heterogeneous media during manufacture and storage and also in the organism:[14,58,100,102-109]

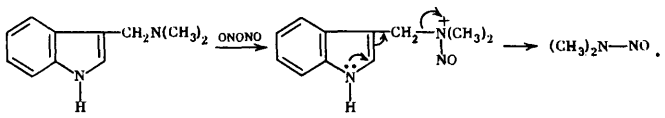


It is assumed that the high rate of this reaction is caused by the presence in the molecule of the "active" dimethylamino-group.[21,15,104] In the medicinal forms of amidopyrine, especially in tablets, the distribution of NDMA is not homogeneous: the greatest amounts are contained on the surface, which can be explained by the action of nitrogen oxide present in air within industrial and storage buildings.[58,104,110] Even the introduction of nitrosation inhibitors does not fully prevent the formation of NDMA.[58,104,106]

Tetracycline, penicillin, etc. react vigorously with nitrosating agents.[86,102,103,109] Other medicinal drugs and metabolities, for example, phenacetine, imizine, and aminazin, are also capable of "nitrosative deamination".[14,100,102,106-111]

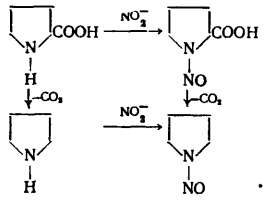
Alkaloids containing the dimethylamino-group can be a source for the formation of NA. This process has been studied in detail in relation to gramine and hordenine—the alkaloids present in barley malt used in the manufacture of beer.[23,27,101] The rate of reaction, which proceeds in accordance with the mechanism proposed by the authors, is close to the rate of nitrosation of dimethylamine, which

can be explained by the presence of the active dimethylamino-group in the gramine molecule:[27,101]



Hordenine is nitrosated much more slowly.[27,110]

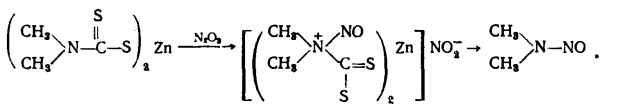
It is also possible to obtain NA from certain aminoacids and the reaction can occur via two main pathways:



In the nitrosation and decarboxylation of aminoacids such as arginine and ornithine, NPyr and NPip have been detected. The ease of formation of NA from aminoacids is attributed to the capacity of the latter for decarboxylation; for example, proline and its derivatives are effectively nitrosated.[24,93,112]

NA are formed also from certain insecticides, pesticides, and herbicides. The dimethylammonium salts of various acids, for example, 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4-DB (2,4-dichlorophenoxybutyric acid), 2,3,6-TCBA (trichlorobenzoic acid), MCP (4-chlorotolyloxyacetic acid), MCPP [2-(4-chloro-2-methylphenoxy)propionic acid], etc., are especially readily nitrosated.[96,103,107,113-115]

The "nitrosative deamination" of a series of pesticides and herbicides containing dialkylamino-group leads to the formation of NA:[95]



NDMA has been isolated from the products of the nitrosation of thiram(tetramethylthiuram disulphide) and ferbam [tris(dimethylcarbamodithioato-*SS'*)iron], NDPA has been isolated from trifluralin (ααα-trifluoro-2,6-dinitro-*NN*-dipropyl-*p*-toluidine), isopropalin (2,6-dinitro-4,*NN*-tripropylaniline), and nitrosobutylethylamine has been obtained from benefin (*N*-butyl-*N*-ethyl-ααα-trifluoro-2,6-dinitro-*p*-toluidine).[95,96,103,113,115,116] The pesticides which are quaternary ammonium compounds and derivatives of morpholine afford NA on interaction with nitrites.[96,103,107,114,117]

Certain products, widely used in the rubber industry, for example, vulcanisation accelerators and stabilisers, are capable of "nitrosative deamination". This applies mainly to substances containing the dialkylamino-group and to derivatives of morpholine.[38,71,99,118-121]

3. Catalysis and Inhibition of the Nitrosation Reaction

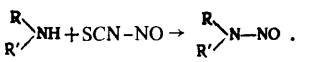
The rate of nitrosation depends on a number of factors among which the structure, basicity, and concentration of the nitrogen-containing compounds to be nitrosated, the properties and concentration of the nitrosating agent, the pH of the medium, temperature, the homogeneity of the reaction mixture, the nature of the solvent, and also the presence of catalysts or reaction inhibitors are important. The rate of reaction of various aliphatic amines with nitrites in weakly acid aqueous solutions is proportional to the concentration of the amine and the square of the concentration of nitrous acid. The kinetics of such reactions have been examined in detail.[21,32,34] The concentrations of the non-protonated form of the amine and of free nitrous acid are of decisive importance for the rapid occurrence of the reaction. The maximum rate of nitrosation of secondary amines with a high or moderate basicity, from which carcinogenic NA are usually formed, has been noted at pH close to 3.4, which corresponds to the dissociation constant of nitrous acid.[21,34,122-124] With increase in pH, the rate of reaction falls (approximately by an order of magnitude for each pH unit), but the NA are formed also at pH 5–6, while in the presence of promoting agents and certain micro-organisms, they are formed at pH > 7.[22,29,34,47-49,123] At low pH, a decrease in the rate of nitrosation was observed as a consequence of the fall in the concentration of the non-protonated form of the amine. For weakly basic amines, a decrease in pH affects less markedly the rate of their nitrosation since under these conditions the concentration of the non-protonated form of the amine is also considerable.[21,34,102]

The rate of formation of NA from amines decreases in the following sequence: morpholine > pyrrolidine ⩾ piperidine > dimethylamine > diethylamine > di-n-propylamine ⩾ di-isopropylamine.[23,33,34,102]

In real objects and in the organism, the conditions for the occurrence of nitrosation are less favourable than in solution but prolonged interaction of the reactants can lead to the accumulation of significant amounts of the NA. In this case the presence of a catalyst or inhibitors of the nitrosation reaction in the reaction medium acquires decisive importance.[5,6,10,81,125-127] The accelerating or retarding effect depends on the reaction medium; certain compounds, for example, phenols, can exhibit the opposite influence under different conditions.

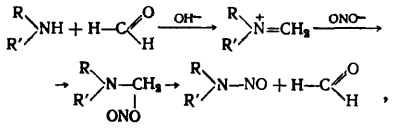
(a) Catalysts. A considerable number of compounds catalysing nitrosation are known.[4,5,10,47,59,115,125,126,128,129] Nucleophilic anions such as thiocyanates and halides are capable of accelerating this reaction significantly.[47,125,126,129-131] In terms of their activities, they can be arranged in the sequence $SCN^- > I^- \geqslant Br^- > Cl^-$.[21,126,131] In the case of SCN^-, the reaction proceeds via the formation of the fairly stable nitrosyl thiocyanate:[55,59,69,126,129,130,132]

$$HONO + SCN^- + H^+ \rightleftarrows SCN{-}NO + H_2O,$$



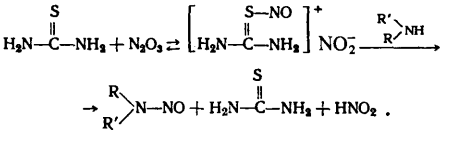
The thiocyanate accelerates this reaction at low pH in solution and also in various objects and in the organism.[47,126,130,132] The I^- ion is an effective nitrosation catalyst; its activity is manifested under different conditions, including heterogeneous nitrosation with nitric oxide.[42,47,126,131] In the presence of I^- and also Br^- and Cl^-, nitrosation proceeds via the formation of nitrosyl halides.[31,47,131]

A number of carbonyl compounds accelerate the synthesis of NA. Formaldehyde shows the highest efficiency; chloral, benzaldehyde derivatives, pyridoxal, mabnodialdehyde, hexachloro- and hexafluoro-acetones, etc. are also active.[28,47,52,125,133] The proposed mechanism of the reactions occurring with participation of carbonyl compounds at pH ⩾ 7 includes the formation of iminium ions:[4,47,52,133]

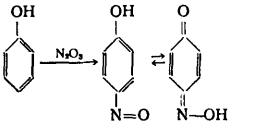


Other substances evolving formaldehyde or reacting analogously probably also catalyse the nitrosation reaction.

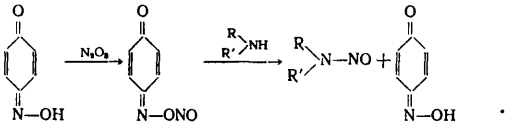
The compounds capable of accelerating this reaction include thiourea and certain thiols.[47,66,130,134] In the case of thiourea, which catalyses the nitrosation of secondary amines at a pH of about 4.0, the reaction proceeds via the *S*-nitroso-adduct:[47,134]



The situation is more complicated with phenols and certain other OH-containing substances which are capable of exerting both catalytic and inhibiting influences on the nitrosation reaction depending on the structure, the pH of the medium, etc.[42,47,66,69,80,135-138] Phenol reacts rapidly with nitrosating agents, for example, with HNO_2, at pH < 4:[47,135]



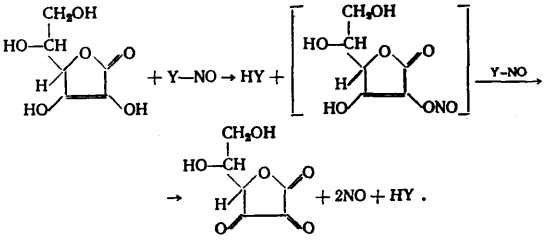
Quinone monoxime is rapidly nitrosated, probably affording the *O*-nitro-derivative, which reacts with the amine:[47,66,135-137]



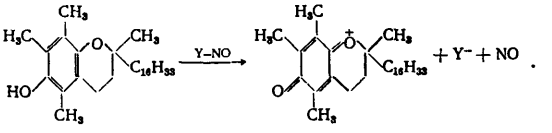
The catalytic action of resorcinol can be explained analogously.[80,135,139] In principle, under certain coditions catechol and hydroquinone can exhibit an accelerating effect;[47,138] however, the probability of their nitrosation is low, since they show a greater tendency to form the corresponding benzoquinones under these conditions.[80,135,138] Other compounds containing the OH group, for example gallic and chlorogenic acids, camphorol, and quercetin, can likewise catalyse the formation of NA.[32,135]

The ability to accelerate the nitrosation reaction has also been discovered in certain unsaturated compounds, surfactants, conjugate bases of bile acids, etc.[32,140] We may note that certain species of micro-organisms are able to accelerate significantly the formation of NA.[47,74]

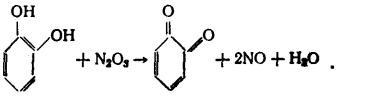
(b) Inhibitors. A large number of compounds able to inhibit the formation of NA have been described.[4,5,12,21,47,106,115,125,126] Naturally, the retardation of the reaction is achieved most simply by altering the conditions and in the first place the pH. This is difficult to achieve in various objects and in the organism. For this reason, much attention has been devoted to the search for effective inhibitors and the determination of the mechanism of their action. Virtually all the compounds proposed for this purpose show an inhibiting influence on the reaction as a result of the inactivation of nitrosating agents, but this can be achieved in different ways. Many substances inhibiting the formation of NA react with nitrosating agents, reducing them to the relatively inactive nitric oxide. Most studies have probably been devoted to ascorbic acid and its derivatives, which are able to inhibit effectively in this way the nitrosation reaction over a wide pH range:[6,46,47,55,68,81,106,115,140-144]



Ascorbic acid is especially active in hydrophilic media. The use of α-tocopherol in hydrophobic media has been recommended:[47,81,115,140,142,143,145]



Together with α-tocopherol, one can also use ethoxyquin (6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline) and dihydroethoxyquin.[146] The oxidation of catechol, hydroquinone, and derivatives of gallic acid and polyphenols, which have been proposed as inhibitors, capable for forming *o*- and *p*-benzoquinones, proceeds via the same pathway:[47,55,69,80,120,135,138,139]



Sulphur dioxide and the bisulphite ion reduce the nitrosating agents to nitric or nitrous oxide:[32,115]

$$SO_2+N_2O_3+H_2O\rightarrow 2NO+H_2SO_4,$$
$$SO_2+2NO+H_2O\rightarrow N_2O+H_2SO_4.$$

Hydroxylamine, various hydrazines, sodium azide, and certain other reductants retard analogously:[33,47,115,147,148]

$$NH_2OH+Y{-}NO\rightarrow N_2O+H_2O+HY,$$
$$NH_2NH_2+Y{-}NO\xrightarrow{H^+}N_2O+NH_4^++HY,$$
$$N_3^-+Y{-}NO\rightarrow N_2O+N_2+Y^-.$$

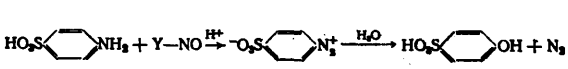
Certain alcohols, for example, ethanol and ethylene glycol, carbohydrates (glucose, sucrose), and other compounds containing the OH group inhibit the formation of NA, being converted into the corresponding alkyl nitrites:[42,78,144,149-152]

$$ROH+Y{-}NO\rightarrow RONO+HY.$$

Thiols react analogously but more vigorously:[57,144,149,150]

$$RSH+Y{-}NO\rightarrow RSNO+HY.$$

The substances examined inactivate nitrosating agents, converting them into the less reactive esters (thioesters) of nitrous acid or nitric (nitrous) oxide. In order to prevent the reactivation of nitric and nitrous oxides, it is essential to use high concentrations of the inhibitors, in particular ascorbic acid and tocopherol.[141,145,153] It is more useful to seek inhibitors converting active nitrosating agents into substances incapable of reacting with amines. The possibility of using derivatives of primary aromatic amines, for example, sulphanilic acid and sulphanilamide, which give rise to diazo-compounds on reaction with nitrosating agents, has been established:[118,141,154,155]



There is no doubt that new effective nitrosation inhibitors can be found among other readily diazotising compounds.

Urea and sulphamic acid, proposed for the retardation of the formation of NA, also lead to the decomposition of nitrosating agents;[47,81,106,115,144,147]

$$O{=}C(NH_2)_2+2Y{-}NO\rightarrow 2N_2+CO_2+H_2O+2HY,$$
$$NH_2SO_3H+Y{-}NO\rightarrow N_2+H_2SO_4+HY.$$

The use of ammonia, tannin, vanillin, thymol, squalene, pyrrole, glutathione, indole, etc. as inhibitors has also been indicated.[6,21,47,69,126,139,153]

It is useful to employ inhibitors to prevent the pollution of various objects by nitrosamines and the formation of these carcinogens in the organism.

III. PROPERTIES OF *N*-NITROSAMINES

1. Physical Properties

The NA considered are oily liquids or solids which are moderately soluble in water and readily soluble in many organic solvents: methylene chloride, chloroform, carbon tetrachloride, ether, alcohols, acetone, dimethyl sulphoxide, dimethylformamide, etc.; they are highly volatile and can be steam-distilled.[1,3,8,32]

The IR spectra of NA have characteristic absorption bands. Thus $\nu(N{=}O)$ for a series of dialkylnitrosamines is in the range 1425 to 1470 cm^{-1}, while $\nu(N{-}N)$ is in the range 1010–1150 cm^{-1}.[3,32,50]

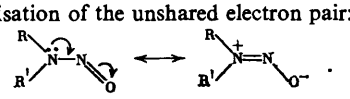
Two maxima, which in the case of aqueous solutions are in the ranges 230–235 nm ($\varepsilon \cong 7000{-}8100$) and 330–350 nm ($\varepsilon \cong 100$), have been found in the UV spectra of NA.[1,3,8,50] It has been noted that the positions of the bands in the IR and UV spectra of NA depend significantly on the nature of the solvent.[32,50]

Fairly intense ions have been observed in the mass spectra of NA obtained on electron impact: the molecular M^+ ion and the fragment ions $M^+ - 17$ (OH split off), $M^+ - 30$ and $M^+ - 31$ (NO or NOH split off), and also an ion with m/z 30 (NO^+). In the mass spectra obtained on chemical ionisation, the maximum content is that of the $(M+1)^+$ ion.[9,156-158]

The bond lengths in aliphatic NA have been determined. Thus in NDMA the length of the N–O bond is 123 nm, while N–N bond length is 134 nm instead of 145 nm, which is the N–N in compounds where both nitrogen atoms are linked to carbon.[31,32] The N–N bond dissociation energy in NDMA is about 55 kcal $mole^{-1}$, which is higher than in nitrodimethylamine.[3,32,50]

The stability of NA is fairly high, exceeding that of nitrodialkylamines. They are not cleaved with solutions of alkalies and dilute acids and are hardly decomposed by scattered light.[3,22,32] These properties of NA predetermine the duration of their presence in the environment.[7,10,13]

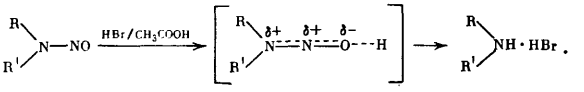
The dipole moments of many aliphatic NA are 3.9–4.4 D, which indicates the polarity of their molecules, determined by the possibility of the delocalisation of the unshared electron pair:[32,50,159]



2. Chemical Properties

The structure and the comparatively high mobility of the π electrons in the molecules are responsible for the fairly high reactivity of NA. They can be protonated, can form hydrogen bonds with alcohols and phenol, can combine with certain substances, for example, alkyl halides, can form complexes with various salts, etc.[22,32,50,159] Many of these processes are of not only theoretical but also practical interest. In principle, all the reactions of NA can be divided into two large groups—occurring with and without the cleavage of the N–N bond. In many cases the interaction of NA with a particular reactant can proceed via both these pathways depending on the conditions.

(a) Denitrosation of NA by inorganic acids. This reaction has attracted much attention by investigators, since the products of the denitrosation of NA are non-toxic and the amines formed have been used to develop methods for the analysis of NA. As already mentioned, dilute solutions of inorganic acids interact with NA very slowly. Thus NA distil from 0.1–0.2 M sulphuric acid almost without decomposition.[9,22,141,155,160,161] With increase in acid concentration cleavage of the N–N bond is accelerated; its completion requires heating of the reaction mixture or the use of catalysts, for example, Cl^-, Br^-, and SCN^-.[22,162,163] NA are most readily denitrosated by HBr solutions in glacial acetic acid; at room temperature, a virtually quantitative yield of the corresponding secondary amines is attained after several minutes:[12,163-166]

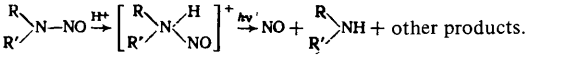


In the presence of small amounts of water or alcohol, the rate of denitrosation decreases significantly.[166,167] An excess of glacial acetic acid with phosphoric (or sulphuric) acid, containing I^- or Br^-, and also HBr solutions in acetic anhydride can denitrosate NA in the presence of water.[167,168]

Various inorganic acids as well as their derivatives, for example, acetyl, oxalyl, and thionyl chlorides are less effective when HBr is the denitrosating agent.[163,164]

(b) The effect of UV light, γ-radiation, and heat. It is possible to cleave to cleave the N–N bond on treatment with UV light or γ-radiation. These reactions proceed via a fairly complex mechanism and not all the intermediates have yet been identified reliably.[124,169-174] It has been noted that the reaction takes place comparatively slowly.[43,171]

Acids and oxidants have an accelerating effect on the cleavage of NA by irradiation with UV light. Several possible pathways leading to the denitrosation of NA on treatment with UV light and acid have been proposed,[165,170,171,175-177] for example:



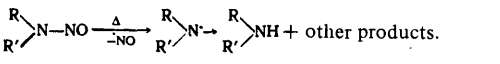
Under certain conditions, this reaction can afford high yields of secondary amines and NO (NO_2^-).[172,175] Account must be taken of the fact that the presence of high NO_2^- or NO_3^- concentrations in the reaction mixture creates favourable conditions for the denitrosation of secondary amines.[170,171]

The action of UV light on NA solutions in the presence of bases also leads to the dissociation of the N–N bond.[165,169]

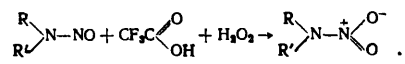
When aqueous solutions of NPip are exposed to the action of γ-radiation in the presence of added acids or alkalies, the cleavage is hindered in the presence of high concentrations of nitrates or nitrites.[42,44,45,178,179]

γ-Irradiation of food products leads to the partial decomposition of the NA contained in them.[45,178,179]

NA are hardly decomposed on heating to 200–250 °C. However, their pyrolysis takes place at 450–500 °C:[124,180-182]

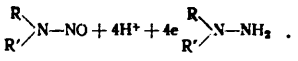


(c) Oxidation and reduction. The interaction of NA with oxidants or reductants can lead to the formation of the corresponding nitramines and asymmetric hydrazines or to the cleavage of the N–N bond. The oxidation of NA without dissociation of the N–N bond is achieved mainly with the aid of peracids, among which CF_3COOH is the most convenient. It is usually obtained directly in the reaction mixture from trifluoroacetic acid and hydrogen peroxide:[165,166,180,181,183]

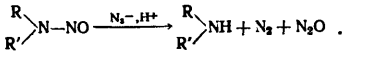


Treatment with pentafluorobenzoic acid and with a mixture of ammonium persulphate and nitric acid, as well as electrochemical oxidation, etc. lead to analogous results.[22,184,185] On treatment of NA with $K_2Cr_2O_7$ or $KMnO_4$ in concentrated sulphuric acid, ozone, etc., the N–N bond is cleaved.[165,166,176]

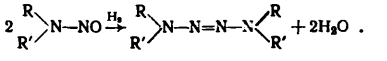
The reduction of NA with zinc in acetic acid to the corresponding dialkylhydrazines has been known for a long time,[50] the same compound being obtained on treatment with $LiAlH_4$, KOH + Al, titanium trichloride, sodium amalgam, etc.[50,186-188] and on electrochemical reduction:[165,186,187]



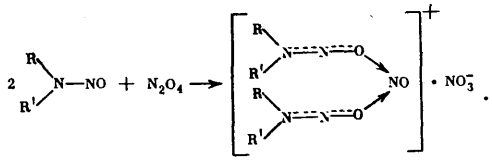
When other reductants are used and the conditions are altered, NA can be converted into mixtures of the corresponding asymmetric hydrazines and secondary amines or mainly into secondary amines. The latter are formed in fairly high yields in the presence of Raney nickel, in an acid solution of copper monochloride or iron dichloride, in the presence of a mixture of nickel, aluminium, and potassium hydroxide, aluminium amalgam, azide, etc.:[165,187]



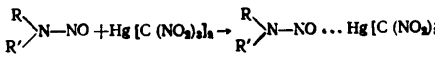
The reduction of NA results in the formation of tetra-alkyltetrazenes in addition to hydrazines and secondary amines:[165]



(d) Complex formation and addition reactions. The delocalisation of the electron pair >N=N=O characteristic of NA predetermines their tendency towards reactions involving the formation of *O*-complexes on treatment with BF_3, PCl_5, $SbCl_5$, $AlCl_3$, etc.[32,50,159] The interaction of NA with nitrogen tetroxide probably proceeds via the mechanism[50,87]

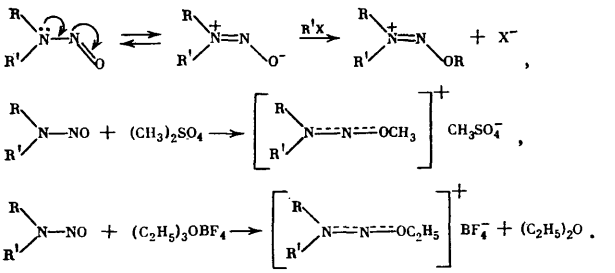


NA can combine with various metal salts, for example $CuCl_2$, $ZnBr_2$, $PdCl_2$, etc. A stable complex is formed as a result of the reaction of NA with bis(trinitromethyl)mercury:[32,50]



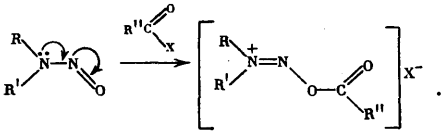
Complexes of NA with bromoplatinic acid and certain other compounds have been described.[32,50]

NA react with many alkylating agents—alkyl halides, dimethyl sulphamate, triethyloxonium fluoroborate, etc.:[159,165,166]

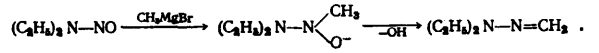


The last reaction proceeds very readily; the resulting salt is involatile and is decomposed by potassium hydroxide, which is used to decompose NA.[165]

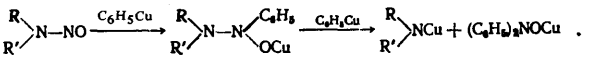
NA react with acylating agents:[32]



Certain reactions of NA with organometallic compounds—a Grignard reagent or CH_3LI—have been described:[22,32,165]



The interaction of NA with phenylcopper takes place with dissociation at the N–N bond:[22,32]



3. Effect on the Organism

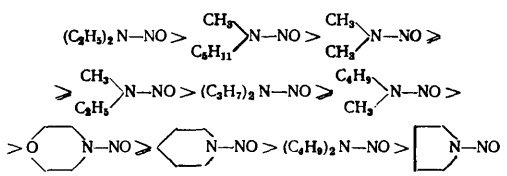
NA exhibit a pronounced toxicity, in the first place in relation to the liver and kidneys, and can give rise to haemorrhagic centrilobular necroses accompanied by blood effusions, the proliferation of bile ducts, disturbance of the renal function, etc.[1-5,8,15,17]

NDMA is the most toxic, its LD_{50} value amounting to about 30 mg kg^{-1} of body weight after single administration to rats. Other NA are less toxic; thus the LD_{50} for NPip, NDEA, and NDPA are respectively 200, 220, and 480 mg kg^{-1}.[1-4,8] Many NA exhibit pronounced mutagenic and carcinogenic activities.[1-4,8,10,14,102,189-192]

According to Shabad's classification,[193] NA are powerful carcinogens. The blastomogenic properties of NA have been investigated extremely widely and have been demonstrated on 40 different animal species: monkeys, dogs, rabbits, pigs, hamsters, rats, mice, guinea pigs, etc. and also on various birds, amphibia, and fish.[1-4,8,10,16] Despite the considerable species differences, the character of the tumours induced by the corresponding NA is similar as regards location and morphological structure. For example, NDMA and NDEA induce liver tumours—cholangio- and haepato-cellular carcinomas. The species-specific blastomogenic activity of NA is much wider than that of all other known chemical carcinogens, which is important indirect evidence for the carcinogenic activity of NA in relation to man.[2-6,8,10,14,102,189,194-198]

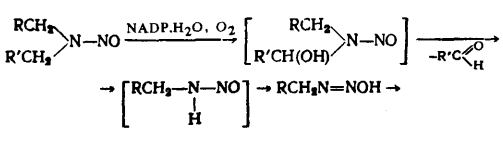
NA exhibit a broad spectrum of carcinogenic activity and can induce the formation of tumours in the liver, kidneys, stomach, alimentary tract, lungs, bladder, trachaea, throat, nasal cavity, etc.[1-5,8,10,17,20,102,199] It is significant that tumours arise both on treatment with NA and when their non-carcinogenic precursors—amines and many nitrogen-containing substances—enter the organism together with nitrosating agents.[3-6,8,10,13,14,16,102,197,200] The formation of NA from precursors has been demonstrated by chemical analysis.[76-79,100,102,105,106,114,200] Micro-organisms capable of converting nitrates and various nitrogen-containing substances into amines and of promoting the formation of NA over a wide pH range including pH $\geqslant$ 7 play an appreciable role in the endogenic synthesis of NA.[3-5,8,10,16,47,199]

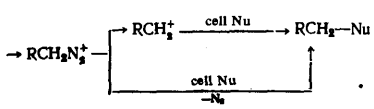
A direct dependence of the blastomogenic effect on the size of the dose and on the duration of its action on the organism has been discovered for NA.[1-5,20,201] It has been suggested that the minimum carcinogenic dose of NDMA for rats is about 0.1 mg per kilogram of body weight per day.[1,10,181] Relatively small frequently non-toxic doses of NA can induce the formation of tumours in various organs in animals and the majority of NA have a carcinogenic effect after a single administration.[1,3,16,20] The relative carcinogenic activities of NA have been calculated from determinations of the NA dose used in the formation of tumours in 50% of animals:[32,194]



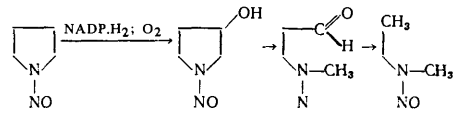
It has been shown that carcinogenic activity is exhibited not by the NA themselves but by the products of their metabolic activation under the influence of enzymes—non-specific microsomal demethylases and oxidases located in the membrane of the endoplasmic reticulum of the cell and catalysing the conversions of NA in the organism, especially in the liver.[1-3,10,16,82,192,202-208]

The metabolism of NA, in the first place NDMA and NDEA, has been investigated and the relation between the products of the biotransformation and the carcinogenic activity has been discovered. These are usually multistage processes which lead to the formation of a number of intermediate and final carcinogens.[2-4,10,14,82,195,196,202,207,209] Although the nature of all the products has not been fully elucidated, it has been suggested that the carcinogenic activity is due to the presence of active centres capable of acting on DNA, RNA, protein, etc. macromolecules in the cell.[4,10,14,16,195,196,204,205,207,209] From the chemical point of view, the reactions of NA in the organism are processes involving oxidative hydroxylation and the cleavage of the hydroxyalkyl derivatives formed under these conditions.[2,3,204,205] It is assumed that the hydroxy-group can be incorporated in various positions, for example, in the α-, β-, and ω-positions in the alkyl groups of the NA. The following mechanism has been proposed for the primary activation of NA by α-hydroxylation:[4,192,202-205]

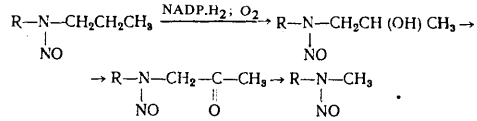




The electrophilic compounds $RCH_2N_2^+$ and RCH_2^+ interact actively with various nucleophiles, in particular with DNA. It has been suggested that the enzymic activation of cyclic NA begins with the cleavage of the ring and the formation of the dialkyl-NA:[205,210,211]



Enzymic β-hydroxylation can proceed as follows:[203-205,210]



Together with processes involving the metabolic activation of the NA, their inactivation reactions also takes place in the organism.[4,16,202,205] The action of the NA on the organism is determined mainly by the alkylation of DNA by the products of their metabolism, which can lead to the breakdown of the functioning of the cell genome. The *N*(7)-, *N*(3)-, and *O*(6)-positions in guanine, and the *N*(7)-, *N*(3)-, and *N*(1)-positions in adenine are most often alkylated.[3,4,14,189,195,196,203-208,212,213] It is believed that the alkylation of the DNA guanine in the *O*(6)-position is significant for the appearance of tumours and the mutagenic effect. Such alkylation damages DNA and disturbs the transfer of genetic information.[4,82,189,195,196,21

Data demonstrating the accelerating or retarding effect of a number of substances, for example, ethanol, hydroxybutylanisoles, and luminal on the NA metabolism have been obtained.[152,201,206,213,214]

It has been shown that there is a clear-cut correlation between the carcinogenic and mutagenic activities of the products of the NA metabolism, but a relation between toxicity and carcinogenic activity has not been established.[14,102,189-192] It has been suggested that the formation of NA from precursors directly in the organism is important in the genesis of cancer.[4,10,14,153,197,215] It is therefore essential to take into account the circulation in the environment and the possibility of the entry into the organism of not only the NA themselves but also of the precursors.[7,216]

IV. PRINCIPAL METHODS OF MICROANALYSIS

The determination of carcinogenic NA in objects within the environment at the microgram and nanogram level is an extremely complex analytical problem, because such objects can contain an extremely large number of substances. For example, thousands of main and hundreds of thousands of minor components have been detected in food products.[198,217]

The main requirements which must be met by the analytical methods for NA are high sensitivity, satisfactory selectivity, and reliability of the results. The determination of NA in objects usually includes all or the majority of the following stages: isolation, preliminary purification, concentration, additional purification, preparation of derivatives, analysis and confirmation of the results. The isolation and purification are the decisive stages ensuring to a large extent the success of the analysis. The methods used to carry out these stages have been examined in a number of studies.[124,141,160,161,180,181,196,218-221]

The methods for the determination of NA makes it possible to analyse them directly or on the basis of their rection products. Spectrophotometric, fluorimetric, polarographic, chromatographic, chromato-spectrometric, and certain other methods have been

proposed for the analysis of NA in solutions and extracts from various objects.[5,12,180,181,186,218] As a rule, methods involving chromatographic separation are used nowadays.

Gas–liquid chromatography (GLC) with different columns, phases, and detectors is frequently employed to identify and determine quantitatively NA. Although NA can be analysed with the aid of flame-ionisation detectors, it is more desirable to use nitrogen-sensitive detectors—thermoionic, conductimetric, and microcoulometric.[12,160,161,180,186,218,222,223] Packed and capillary columns filled with various stationary phases, for example, 10–15% Carbowax 20 M on Chromosorb G or W, 5% Carbowax 20 MTPA on Supelcoport, 2–3% OV-1 on Chromosorb G or W, 5% SE-20 on Chromosorb G or W, and UCON-HB 5100 CPWAX57CB are used for the separation. Chromatography under isothermal conditions is rarely used, the temperature being usually programmed in the range 50–200 °C at a rate of 2–10 K min^{-1}. The quantitative determination is carried out as a rule with an intenal standard; the detection limit is at the level of several nanograms.[9,180,186,218,219,221,224-227]

The retention times of NA, especially NDMA and NDEA are short, and their peaks are distributed in the region of the chromatogram with a high content of peaks due to various volatile substances from the object analysed, which hinders their identification. The NA isolated from the object must therefore be carefully purified before the GLC. In a number of cases, even under the conditions of thorough purification, the agreement involving the retention times does not yet guarantee the reliability of the results of the determination.[9,180,186,218,225]

A novel chemiluminescence method for the analysis of NA was proposed in 1975 and a special apparatus—a thermoenergetic analyser (TEA)—was constructed.[55,99,114,117,124,181,182,196,219,220,228-231] Its operation is based on the decomposition of the NA in a catalytic pyrolyser at a temperature in excess of 450 °C. The NO· radical formed under these conditions interacts with ozone. The reaction results in the appearance of an excited NO_2^*, which passes to the ground state with emission of the characteristic radiation in the IR part of the spectrum, after which it is recorded with a photoelectron multiplier:

$$\mathrm{R_2N{-}NO} \xrightarrow{\Delta} \mathrm{R_2N^{\cdot}} + \mathrm{NO^{\cdot}},$$

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2^*} + \mathrm{O_2},$$

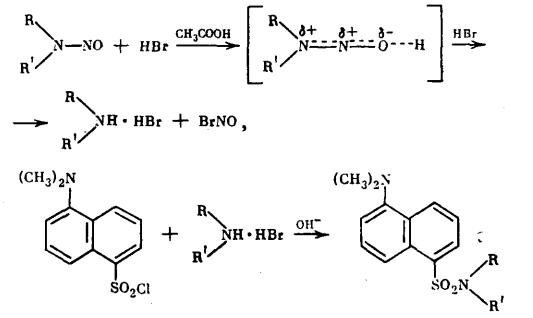
$$\mathrm{NO_2^*} \rightarrow \mathrm{NO_2} + h\nu .$$

In the main TEA is used as a specific detector for NA in combination with various chromatographs. In terms of its analytical parameters, the TEA method is greatly superior to other detection methods in GLC; the detection limit on the TEA is less than 1 ng.[38,55,99,124,180-182,196,219,220,226,232-235] This has ensured a wide-scale application of GLC with TEA for the determination of NA in various objects within the environment despite the fact that certain other NO- and NO_2-containing substances, for example, *C*-nitroso- and *C*-nitro-compounds as well as *O*-nitroso- and *O*-nitro-compounds, can give rise to false positive results.[124,180,181,196,218-220,225,228,235,236] NA have been determined most reliably in different objects by the chromato-mass-spectrometric method.[9,12,158,172,173,186,224,235,237-239] The application of a high-resolution mass-spectrometer with electron impact ionisation makes it possible to record one, most specific ion. In NA analysis, this ion is as a rule M^+ or NO^+.[157,181,183,219,235,237] It is somewhat more difficult to identify NA on the basis of low-resolution mass spectra. In this case selected ions are monitored. The presence of NA is regarded as established if the mass spectrum of the chromatographic peak with the corresponding retention times contains all the selected ions characteristic of the given NA and their intensity ratios are close to the ratios in the mass spectrum of the standard.[9,157,180,181,183,219,224,235,237] Chromato-mass-spectrometric methods of determination, especially at low resolution, require careful purification of the extracts, since the selected ions are in the region of low masses mixed with fragments of other compounds present in the extract.[9,141,218,219,224] The use of mass spectrometry with chemical ionisation is effective in the determination of NA.[9,156,157,240]

A series of GLC and chromato-mass-spectrometric methods have been proposed for the analysis of NA on the basis of their reaction products. The determination of NA after their oxidation to the corresponding nitramines, having longer retention times than the NA with detection based on electron capture or mass spectrometrically with the aid of TEA has been described.[12,180,181,183,186,219,225] The method is used rarely because of its inadequate reproducibility. Chromatographs with an electron impact detector and chromato-mass-spectrometers are used to determine NA after their conversion into halogeno-derivatives, which are frequently obtained on treatment with heptafluorobutyryl chloride or heptafluorobutyric anhydride:[12,122,180,181,183,184,186,219,223,225,241]

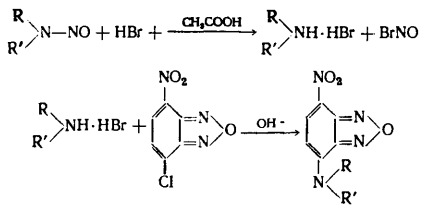
$$\mathrm{R_2N{-}NO} + \left(\mathrm{C_3F_7C}\overset{\mathrm{O}}{\diagup}\right)_2\mathrm{O} \xrightarrow{\text{pyridine}} \mathrm{R_2N{-}C(O){-}C_3F_7}.$$

A method based on the use of dansylamides, obtained from NA by treatment with 1-dimethylaminonaphthalene-5-sulphonyl chloride, is effective for the analysis of NA in various objects:[9,155,225,237,242]



The mass spectra of the dansylamides obtained from various NA contain intense molecular and fragment ions which are either common to all the derivatives, for example the $(NH_3)_2NC_{10}H_7^+$ ion with *m/z* 171 or are characteristic of individual compounds (formed on dissociation of the S–N bond), which makes it possible to identify and determine the NA.[9,155,237,242] The monitoring of selected ions has proved optimal for the detection of dansylamides. The recording of a chromatogram based on several such ions, the retention times as well as the ratios of the intensities of the mass-spectral lines and the areas of the corresponding peaks ensure a reliable identification of the compound analysed; the detection limit is less than 1 ng.[9,155,237,242] The selected ions in the mass spectra of dansylamides are in the region relatively free from ions of impurities present in the NA extract, which makes it possible to employ low-resolution mass-spectrometers and does not necessitate a careful purification of the extract.[9,141,237,242] The adequacy of the standards obtained from the NA and the corresponding secondary amines has been established; the use of the latter simplifies the analysis and makes it safer.[141,155,237,242-244]

The chromato-mass-spectrometric method based on the preparation of NBD-amines by treatment with 7-chloro-4-nitrobenzo-2,1,3-oxadizole is entirely suitable for the analysis of NA:[155,225,243,245]



The mass spectra of NBD-amines contain intense molecular and characteristic fragment ions which can be effectively determined by monitoring the selected ions. The possibilities of this method are analogous to the method involving the use of dansylamides.[155,225,245] The chromato-mass-spectrometric methods for the determination of NA on the basis of their derivatives—dansylamides and NBD amines—can be used also to confirm the results obtained by other methods.[9,141,155,225,237,242,245]

High performance liquid chromatography is used more rarely for the analysis of volatile NA than GLC. The analysis is performed on sorbents: Lichrosorb Si 60, Microporasil, Spherisorb 3SW, Sorbax CN, etc.: the elution is carried out with mixtures of organic solvents, for example, chloroform – cyclohexane – methanol, isopropyl alcohol – hexane, and chloroform – hexane.[124,220,225,229,246] The reversed-phase version on Microbondapak C_{18}, Sorbax ODS, silica gel C_{18}, etc. with mobile phases containing acetonitrile, methanol or ethanol, water, or buffer systems is also used.[173,177,225,227] TEA, photoconductimetric, electrochemical, and UV detectors are used to detect the separated NA; the NA are frequently subjected to preliminary cleavage and are treated with the Griess reagent.[227-229,243,246,247] The detection limit is about 1 ng.[124,173,177,181,220,225] There are data concerning the analysis of NA by the high performance liquid chromatographic method in the form of derivatives.[225,243,247]

A series of simple methods for the determination of NA using thin layer chromatography (TLC) have been proposed. The methods described earlier—involving irradiation with UV light and detection on the basis of the $NO(NO_2^-)$ or R_2NH formed in the form of coloured compounds, are inadequately sensitive and selective.[12,180,186,218,223,225] The methods based on the denitrosation of the NA with HBr and the preparation of fluorescent derivatives of secondary amines have much better characteristics. In principle, different reagents are suitable for this purpose[243,248] but dansyl chloride and NBD chloride are mainly used for the analysis of NA in various objects.[9,141,155,168,218,225,243,244,249] The analysis is performed directly on a plate, visually and densitometrically, or the corresponding spots are eluted and the fluorescence intensity is measured. The detection limit is 1 – 10 ng in the spot.[141,155,168,244,248,249] Compared with dansylamides, the determination of NA in the form of NBD-derivatives is more effective, since the latter not only fluoresce but are also coloured yellow, orange, or pink, while NBD chloride itself does not fluoresce and does not form fluorescent compounds with phenols and alcohols.[141,155,218,241,243,244,248,250] An analogous method has been proposed for the determination of NA in the form of fluorescent derivatives, obtained by the interaction of secondary amines with *N*-(8-methoxyqinoline-5-sulphonyl)aziridine,[251] but in terms of a number of characteristics it is inferior (inadequate separation of derivatives, complexity of the chromatography, etc.) to the method with NBD chloride.

The usefulness of carrying out the TLC in the presence of a control sample from part of the extract after the removal of the NA has been demonstrated. The use of such control samples, which hardly differ in terms of the composition of the impurities from the experimental sample, ensures the reliability of the analysis.[141,155,225,250] The use of comparison samples, prepared by introducing the corresponding standards into the control samples, is even more effective.[252] This procedure simplifies significantly the identification of NA, accelerates the analysis by eliminating the additional purification, and increases the reliability of the determination by reducing the probability of obtaining false results.[252]

It is thought essential to confirm the results of the determination of nanogram and microgram amounts of NA in objects within the environment. Chromato-mass-spectrometric methods are used for this purpose or the analysis is carried out by two different methods.[124,155,172,180,181,184,186,218,219,224,225,233,239,253]

V. THE CONTENT OF *N*-NITROSAMINES IN OBJECTS IN THE ENVIRONMENT

1. Air

Extremely complex processes involving the formation and decomposition of NA take place in the atmosphere. The concentration of nitrogen oxides plays a significant role in the formation of NA. It is believed that the NA content in air is a problem associated with the waste from industrial undertakings, transport, and the pollution of the atmosphere by nitrogen-containing substances.[7,10,54-57,114,216,230] This is confirmed to some extent by the finding that, under conditions remote from large industrial and agricultural manufacturing undertakings, the air contains hardly any NA ($\leqslant 0.01$ μg litre^{-1}).[56,103,114,254] Up to 0.05 μg litre^{-1} of NDMA has been found in the atmosphere over non-industral towns, while the content over industrial towns is 0.76 – 1 μg litre^{-1}.[56,103,114,255] Higher NA concentrations have been observed in chemical, leather, and rubber manufacturing plants: up to 36, 47, and 140 μg litre^{-1} of NDMA and up to 46,20, and 250 μg litre^{-1} of NMor respectively.[55,56,103,114,119,230,254,256] This can be explained by the presence in the above undertakings of a series of readily nitrosated substances, for example, amines and vulcanisation accelerators.[71,99,114,119,121,230,254-257] Other NA may be present in the air within these factories at lower concentrations.[56,99,254,256,258]

The air in showrooms for new automobiles contains the following amounts of NA (in μg kg^{-1}): NDMA $\geqslant$ 1.0, NDEA $\geqslant$ 0.4, and NMor $\geqslant$ 2.5, which can be explained by their evolution from rubber components.[119,121,254,256,259] A series of NA have been found in air within smoking rooms and kitchens, which has been attributed to their presence in tobacco smoke and their evolution in the frying and cooking of food.[55,98,114,183,200]

It is noteworthy that in the atmospheres of towns domestic and tobacco smoke contains significant amounts of nitrogen oxides.[56,78,98,161,255,260]

2. Water

Comparatively little attention has been devoted to the determination of NA in water possibly because they are either absent from purified drinking water or their concentration is extremely low ($\leqslant 0.01$ μg litre^{-1}).[8,13,114,117,241,261,262] Relatively larger amounts are present in chlorinated water (NDMA $\leqslant$ 1.0 μg litre^{-1}) and deionised water (NDMA $\leqslant$ 0.5 μg litre^{-1} and NDEA $\leqslant$ 0.8 μg litre^{-1}).[35,103,114,117,261] NA have been detected in various types of waste water. Thus up to 2 μg litre^{-1} of NDMA has been found in sea water in the vicinity of waste discarding points in a fish processing plant, the discarded water containing NDMA ($\geqslant$3 μg litre^{-1}) and NDEA ($\geqslant$0.2 μg litre^{-1}).[5,114,117,255,261] The waste water from various factories contains up to 10 μg litre^{-1} of NDMA, 5.5 μg litre^{-1} of NDEA,

and certain other NA,[103,114,183,223] while in individual types of water containing slime the content of NA is up to 940 μg litre^{-1}.[128,223] The concentration of NA in waste water containing amines is usually enhanced.[182,252]

In order to prevent the pollution of the environment by nitrosamines, it is essential to purify the waste water, since these carcinogens can pass from water into plants.[7,10,216,222,223,262] Nitrites and nitrates have been detected in natural waters, the concentration of the latter being high.[10,55,255,261]

3. Soil

The turnover of NA in the soil has been inadequately investigated. NA and their precursors can enter the soil from the atmosphere, together with fertilisers and pesticides, with waste water, etc. Although many different amines, other nitrogen-containing bases, nitrates, and nitrites are present in the soil, NA do not usually accumulate in the soil.[5,10,216,262] This can be explained by the occurrence of NA degradation processes under the influence of light, temperature, and the microflora, evaporation into the atmosphere, transfer to water, sorption by plants, etc.[7,10,13,75,216,222,255,262]

4. Inorganic Nitrogen-containing Fertilisers and Pesticides

High concentrations of NA, sometimes exceeding 1000 μg kg^{-1} have been found in a number of pesticides.[8,12,39,96,103,113,114,116,117,183] There is a high content of NDMA in dimethylammonium salts of 2,4-D, 2,4-DB, MCPP, MCP, and TCBA, alkylbenzyldimethylammonium chlorides, cetylethyldimethylammonium bromide, thiram, etc.[96,103,107,115] NMor is present at high concentrations in *N*-alkyl-*N*-ethylmorpholinium ethyl sulphate and NDPA is present in trifluralin (treflan), isopropalin, etc.[96,103,107,114,117]

The presence of NA in inorganic nitrogen-containing fertilisers has not been reported but they are a most important source from which nitrates enter the soil, natural water basins, and plants.[7,10,75,216,263]

5. Products of the Chemical and Rubber Industry

NA have been detected in products produced on a large scale such as amines and solvents. The amines contain the corresponding NA; thus dimethylamine contains up to 17 300 μg kg^{-1} of NDMA, pyrrolidine contains up to 53 000 μg kg^{-1} of NPyr, and dipropylamine contains up to 13 000 μg of NDPA; the concentrations of NA are somewhat lower in other secondary and tertiary amines.[12,183,257]

NMor has been detected in chloroform and methylene chloride at concentrations reaching 376 and 32 μg kg^{-1} respectively. Small amounts of NDMA and NDEA have been found in a number of other solvents. NA are as a rule not detected in these products after purification.[58,264] NDMA, NDEA, and other NA have been found in certain types of synthetic detergents.[14]

Rubber vulcanisation accelerators contain considerable amounts of NA, for example, NDMA (4–800 μg kg^{-1}) in tetramethylthiuram disulphide, (NDEA 10–100 μg kg^{-1}) in tetraethylthiuram disulphide, and zinc diethyldithiocarbamate, NMor (60–3500 μg kg^{-1}) in various morpholine derivatives, etc.[38,71,99,118,119,121,232,253] NA have been discovered also in various rubber articles, including those designed for medical and food related purposes. The contents of NDMA, NDEA, and NMor are 50.3, 2.2, and 120 μg kg^{-1} respectively in medical tourniquets, rubber hose for the milk industry, and certain rubber articles for the food industry prepared by the continuous vulcanisation method.[38,40,118,154,253,259,265] In the rubber teats for babies' bottles, babies' dummies, stoppers for bottles with babies' food, rubber toys, and rubber gloves, the maximum concentrations of NDMA, NDEA, NDBA, NPip, and NMor are 200, 100, 2796, 180, and 86 μg kg^{-1} respectively.[38,40,71,99,118,121,229,232,253,265,266] NA are capable of diffusing from rubber into liquids in contact with it—milk, milk product, fruit juices, etc.[11,38,99,232,253,266] This made it necessary to pay significant attention to reducing the NA content in rubber for food and medical purposes. The introduction of inhibitors into rubber mixtures and the improvement of the technology made it possible to solve this problem.[118,154,174,265]

6. Medicinal Preparations

NA, usually NDMA, have been found in a number of medicinal preparations. For example, amidopyrine contains 1–371 μg kg^{-1} of NDMA, while the content in individual specimens is up to 980 μg kg^{-1} of this NA; there is up to 68 μg kg^{-1} in imizine, up to 40 μg in nitrofurantoin, and up to 7 μg kg^{-1} in oxytetracycline.[12,58,86,102,104,110,183,230] NA have been detected in medicines which incorporate amidopyrine, piperazine, phenacetin, ephedrine, imizine, pipolphen, aminazin, tetracycline, pencillin, analgin, and many others.[14,102,104-106,109-111,230]

It has been shown that many medicinal preparations can be nitrosated directly in the human stomach.[102,106,108]

7. Animal Feed

NA and their precursors are encountered in various types of animal feed. Nitrates, sometimes nitrites, and (only in individual specimens) small amounts of NA have been detected in meadow grass.[231,263,267] Up to 150 mg kg^{-1} of NDMA together with precursors have been found in mixtures of juicy feed together with concentrates and in feed for birds and rabbits.[5,8,102,268]

Various concentrates, including fish meal, in which the NDMA and NDEA concentrations can reach 417–2000 and 36 μg kg^{-1} respectively are used as additives to feeds.[8,128,268,269] NDMA (2 and 85 μg kg^{-1}), NDEA (24 and 512 μg kg^{-1}), and certain other NA have been found in grass and maize silos.[270-272] NA have been discovered in the milk of cows and goats and the eggs of birds receiving feed with a high content of NA and their precursors.[263,268,271] Significant amounts of NDMA, NDEA, NPip, and NPir (up to 79, 65, 300, and 26 μg kg^{-1} respectively) have been detected in the diet of laboratory animals.[8,58,127,231,269]

8. Food Products

The most important food products, prepared dishes and drinks, have now been analysed and in a number of countries systematic monitoring of the NA content in such products has been introduced. NA precursors, in the first place nitrates and nitrites, are determined in many products;[5,7,10,19,40,122,218,273] account must be taken of the fact that the technology of the preparation of many meat products and cheeses provides for the introduction into them of definite amounts of nitrates and nitrites.[11,107,122,127,198,218,274] Much attention has been devoted to the study of the content of amines in food products, although the presence of a broad spectrum of these substances and the necessity for their determination together with nitrates and nitrites was demonstrated as early as 1976.[275] Data

characterising the degree of contamination of food products and drinks by NA and their precursors have been published in a series of monographs and reviews.[3,5,8,10,12,19,23,39,75,122,125,128,148,183,200,215,218,220,276]

As a rule, NA are encountered much more rarely at relatively lower concentrations in raw and cooked products then in fried, smoked, salted, and preserved products. Thus the overall content of NDMA and NDEA can reach 5 μg kg^{-1} only in individual specimens of fresh, freshly frozen, and cooked meat, while the content in cooked sausages can be 10 μg kg^{-1}.[9,122,125,127,160,161,217,233,260,277,278] NA are frequently detected in various types of bacon, large smoked sausages, small smoked sausages, smoked pork products, and preserves, the maximum NDMA, NDEA, NDBA, NPyr, and NPip concentrations amounting to 84, 16, 4, 207, and 50 μg kg^{-1} respectively.[9,40,114,122,125,127,148,160,233,236,265] The amount of NPip increases sharply, sometimes up to 1600 μg kg^{-1}, in smoked products prepared with an excess of spice.[125,127,183,220,279] Nitrosothiazolidine (in an amount of the order of 20 μg kg^{-1}) has been found in bacon and in fried, smoked, and preserved meat. NMor is encountered extremely rarely in food products.[11,236,276,278,280,281] There is a fairly high content of nitrates and nitrites—up to 145 and 750 μg kg^{-1}—in meat products, especially smoked, salted, and preserved products.[40,122,127,148,160,215,233,236,273]

Fish products and sea food are less often found to contain NDMA—up to 9 μg kg^{-1} in individual fresh species. The maximum NDMA, NDEA, NPyr, and NPip concentrations in salt-dried, pickled, smoked, and fried fish can reach 84, 51, 37, and 19 μg kg^{-1} respectively, the frequency of their detection being very high.[3,125,148,160,161,220,234,253,260,265,282] Up to 400 μg kg^{-1} of NDMA [125,128] has been found in salted and salt-dried fish prepared using technical common salt containing nitrates, while hot-smoked fish, obtained using the smoke from wood chips, may contain up to 206.5 μg kg^{-1} of NDMA.[234] Much NDMA (up to 12 600 μg kg^{-1}) has been found in sauces made of sea food (prawns etc.) especially those containing nitrates and nitrites.[183] Apart from nitrites and nitrates, whose concentrations are 30 and 100 mg kg^{-1}, fish and fish products contain amines.[148,160,260]

Milk and plant products are much less contaminated by NA and they contain as a rule only NDMA. NA are almost absent from milk, acid milk products, and curd cheese. However, NDMA and NDEA have been found in dried milk and individual varieties of cheese, for example, Gouda, Cheddar, and wine cheese—up to 68 and 20 μg kg^{-1} respectively.[5,58,122,161,183,215,218,238,250,272,274,277,279] It is noteworthy that the content of nitrites and nitrates in milk and cheeses can reach 1.6 and 76 μg kg^{-1}.[122,218,238,274]

NA are absent from most cereals, vegetables, and fruit; NDMA (2–5 μg kg^{-1}) has been found in stored vegetable and fruit preserves, but the levels of NDMA and NPyr in salt-pickled vegetables reach 63 and 32 μg kg^{-1} respectively.[125,141,148,244,282] As a rule, fruit and vegetables contain a fairly large amount of nitrates, for example, lettuce and beetroot contain up to 8000 mg kg^{-1}.[55,75,148,200,244,282]

NDMA have been found in beer and alcoholic drinks (up to 68 μg $litre^{-1}$ in dark varieties of beer).[6,39,122,148,200,246,277,279,282] It is believed that the NA concentration in beer depends on the quality of the malt.[40,101,233,246,260,277]

Like water, drinks contain nitrates.[55,200] It has been noted that the content of NA, nitrites, and nitrates in the same type of product vary within considerable limits depending on the conditions of their manufacture and storage.[125,127,183,218]

The amount of NA entering daily the human organism together with the diet has been calculated. Naturally, it is different for different countries but it does not usually exceed 2.3 μg per day for man.[3,5,6,10,55,122,148,200,220,277] Significant amounts of nitrates and nitrites enter the human organism together with food products.[6,10,39,55,122,148,200]

Hygienic norms, according to which the limiting permissible NDMA and NDEA concentrations (overall) in various food products must not exceed 2–4 μg kg^{-1} have been specified.†

One of the ways in which food products are contaminated by NA is circulation in food chains. The circulation of NA is a complex process in which account must be taken not only of the transfer of the NA themselves but also of their precursors, capable of forming these carcinogens readily and directly in the given objects. The total NA and their precursors passing from the environment into plants and food products, the formation of NA, and the various reactions of these compounds and their denitrosation determine ultimately their concentration in the given object.[7,126]

Circulation in food chains begins with the contamination of plants by NA and their precursors.[7,10,193,216] It has been shown that NA, nitrites, and nitrates are capable of passing from water and soil and also from residues of inorganic nitrogen-containing fertilisers, pesticides, and industrial and agricultural waste contained in them into plant products and accumulating there.[7,10,216,222,263,267]

Together with various types of feed and water, NA, nitrites, and nitrates enter the organisms of animals and pass into the products of animal husbandry—milk, meat, and eggs.[7,10,216,263,268,271] When various products, especially those with high concentrations of NA precursors, are stored, NA are formed in them.[122,125,128,244,284] Together with food, drinks, and water, NA and their precursors enter the human organism; NA are formed from their precursors in the gastrointestinal tract.[3-5,10,102] It has also been shown that NA can pass into food products from packing materials.[11,281]

The second way in which food products are contaminated is technological treatment: smoking, frying, salting, drying, dry-curing, etc.[40,127,216,233,234,260,284] Much evidence has been obtained showing that high NA concentrations are then observed in products containing considerable amounts of nitrites and nitrates.[10,40,122,127,233,260,273] Smoking using smoke containing nitrogen oxides results in a significant increase of NA levels.[10,160,234,260] It has been shown that a decrease in the concentration of nitrates, nitrites, and nitrogen oxides and also the introduction of inhibitors and the improvement of technology make it possible to obtain smoked, salted, fried, etc. products with a low NA content.[5,40,122,127,198,233,234,273,277]

A decrease in the amount of NA in various nitrogen-containing substances entering the environment as a result of the effective purification of industrial and transport waste and strict regulation of the use of nitrogen-containing inorganic fertilisers, pesticides, etc. is important for the reduction of the degree of contamination of food products by NA.[7,10,216]

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Thus carcinogenic NA are capable of being formed from a wide range of nitrogen-containing substances and nitrosating agents directly in various objects and living organisms. The ease of formation and the fairly high reactivity and stability of NA are responsible for their wide distribution in the environment and the possibility of their undesirable influence on man.

The development of effective and reliable chromatographic methods for the identification and quantitative determination of these compounds in various objects in microgram and nanogram amounts has played an important role in the study of NA. Systematic analyses made it possible to discover objects with a high NA content and the principal causes of their accumulation and to propose certain measures in order to prevent or sharply reduce the contamination of such objects by these carcinogens.

† "Temporary Hygienic Norms for the Content of *N*-Nitrosamines in Food Products", Ministry of Health of the USSR, Moscow, 1986, 13 pp.

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The Preparation, Structure, and Properties of Semiconductor Films Based on Acetylenic Polymers

A.A.Matnishyan

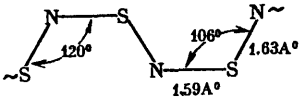
The methods of preparation of organic polymeric semiconducting materials by the catalytic polymerisation of acetylene and its derivatives are described. The characteristics of the catalyst and the influence of the conditions of synthesis on the structure, morphology, stability, and conductivity of the films as well as the questions of the ageing, stabilisation, and doping of the films and the appearance of microheterogeneities (defects) as a result of ageing and oxidation of polyacetylene are considered.
The bibliography includes 196 references.

CONTENTS

I. Introduction 367
II. The synthesis and properties of polyacetylene 367
III. The synthesis and properties of polyacetylene derivatives 371
IV. Copolymers and composites based on polyacetylene 373
V. The oxidation, reduction, doping, and stabilisation of the films 374
VI. The structure and morphology of polyenes 376

I. INTRODUCTION

Organic materials, especially polymers, are already used in electronics, radio engineering, and electrical engineering as electrically conducting and semiconducting elements. After the discovery of semiconducting properties in polymers with a system of conjugated bonds, their investigation has been continuous since the 1950's with continued success.[1-5] The discovery in 1973 of the polymers $(SN)_n$ exhibiting metallic conductivity and not containing metal atoms led to an avalanche of investigations. It was soon found that the polysulphonitrite (polythiazide)



exhibits an intrinsic metallic conductivity and passes to the superconducting state at ~0.3 K.[6] The reports of the first organic polymer capable on doping of the transition from the semiconducting to the metallic state was a well established fact and served as a stimulus for the creation of a series of new conjugated polymers and composites based on polyacetylene, polypyrrole, polythiophen, etc., whose electrophysical properties vary within wide limits during their doping by electron acceptors or donors. However, the high conductivity and effective semiconducting properties of π-electron low-dimensional systems is not their only positive feature; they also manifest various interesting magnetic, optical, and other properties. These materials have begun to play an important role in the development of modern technological systems for the accumulation and storage of information (computers) and the transformation of solar energy,[7] in electronics (field transistors, diodes),[8] and as conductors, electrodes (accumulators, high-capacitance condensers), and as sensors of electromagnetic and acoustic radiation, and also in other branches of engineering.[9,10] The lightness and high strength, characteristic of polymeric materials, their high impact strength, their low cost, and the simplicity of the technology of the preparation of the films, fibres, and articles of complex shape make the new materials advantageous compared with traditional ones.[11]

The synthesis, properties, and applications of polyacetylene have been considered in fair detail in monographs and reviews[1-4,12-18], whose number has increased sharply in recent years.

This paper surveys the results of the latest research into the methods of synthesis and certain properties of polymers of the acetylene series with a regular structure, which are promising as "organic metals" and semiconductors. It deals mainly with the methods which make it possible to obtain films and fibrous materials; it does not include familiar methods such as dehydrogenation, dehydration, and dehydrohalogenation,[19,20] which lead to the formation of films with an irregular structure, exhibiting a low electrical conductivity.

II. THE SYNTHESIS AND PROPERTIES OF POLYACETYLENE

One of the most thoroughly investigated methods of synthesis of polyacetylene (PA) with a regular structure involves the polymerisation of acetylene on a metal complex catalytic system obtained from trialkylaluminium combined with alkoxytitanium. In 1958 Natta and co-workers succeeded in polymerising acetylene in the presence of $Al(C_2H_5)_3-Ti(OC_3H_7)_4$ catalytic system.[21,22] Systematic studies in recent years[23-25] made it possible to find new methods for the synthesis of stereoregular polyacetylene films. The $Al(Et)_3-Ti(OBu)_4$ catalytic system ensures the preparation of PA films with a predominantly (up to 98%) *cis*-structure at temperatures not above 70 °C and with mainly *trans*-structure at +150 °C.[26]

If one disregards the specific requirements which must be met by the conditions in the preparation of the catalytic system (in an inert medium in the absence of traces of moisture), the synthesis of PA itself does not present major difficulties. PA films grow on the surfaces of a concentrated catalyst solution or almost on any support wetted with a catalyst solution (preferably in toluene) in an atmosphere of purified acetylene.[25] The growth of the films can be regulated by altering the temperature and acetylene pressure during the synthesis.[24,27] Before its use, the homogeneous catalytic system is usually maintained at room temperature. The catalyst "ripening" reaction then takes place:[28]

$$Ti(OBu)_4+AlEt_3\rightarrow EtTi(OBu)_3+AlEt_2(OBu),$$
$$2EtTi(OBu)_3\rightarrow 2Ti(OBu)_3+C_2H_4+C_2H_6,$$
$$Ti(OBu)_3+AlEt_3\rightarrow EtTi(OBu)_2+Al(Et)_2OBu,$$
$$EtTi(OBu)_3+AlEt_3\rightarrow EtTi(OBu)_3\cdot Al(Et)_3.$$

The ageing of the catalyst initially increases the activity but after a time the yield PA falls owing to the further reduction of titanium:

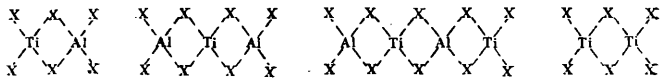
$$EtTi(OBu)_2 + Al(Et)_3 \rightarrow TiOBu + Al(Et)_2(OBu) + C_2H_4 + C_2H_6.$$

If the synthesis is carried out at a low catalyst concentration, a gel-like red product, consisting of tangled fibrils up to 800 Å in diameter, is formed. A foam-like material with a density ranging from 0.04 to 0.4 g cm^{-3} can be obtained from dilute gels by subliming the solvent at a temperature below its freezing point.[29]

The study of the dependence of the rate of formation of PA films on the catalyst concentration and acetylene pressure made it possible to find the optimum ratio of the catalyst components (Al/Ti = 4); the increase of this ratio to 10 increases the size of the fibrils.[30] The fall of the rate of reaction at the end of the process can be explained by the impairment of the diffusion of the monomer through the thickness of the film formed on the catalyst surface.[31] During synthesis, the film is formed simultaneously on the walls of the flask and on the surface of the catalytic solution, the gel accumulating in the upper layer and the PA powder settling on the bottom of the reactor. The molecular weight $\overline{M}_n$ of the powder is lower than that of the gel and decreases with increase in the catalyst concentration to 400–500.[32] The molecular weight of the gel-like PA decreases slightly with increase in the catalyst concentration and rises from 2×10^4 to 3.6×10^4 with increase in temperature from −78 °C to −10 °C. The molecular weight of the PA in the film is a factor of two smaller than in the gel.[33]

The high sensitivity of the catalysts to impurities precludes an unambiguous estimation of the influence of various factors determining $\overline{M}_n$ of polyacetylene. Low-molecular-weight products with $\overline{M}_n \cong 1200$ are formed when the synthesis is carried out in hydrogen.[15] The concentration of acetylene has a considerable influence on $\overline{M}_n$: with increase in its pressure to 760 mmHg, $\overline{M}_n$ increases to 120 000.[28,34] Apparently the inhomogeneity of the substrates, arising from the imperfection of the technique of the synthesis, is the cause of some lack of reproducibility in the properties of the polymers obtained.

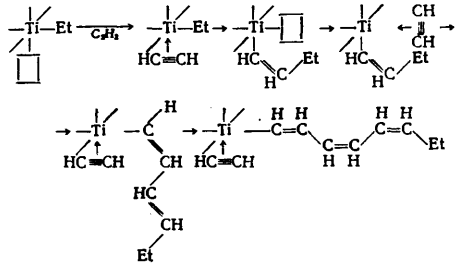
It has been suggested that the synthesis takes place on the "surface" of the catalytic clusters. Investigation by the EPR method made it possible to distinguish up to four types of complexes in the catalyst:[35]



(I) (II) (III) (IV)

The highest catalytic activity is shown by the complex (I), while the complexes (II) and (IV) are inactive. The ratios of the complexes in the catalyst depend on the Al/Ti stoichiometric ratio.

The structure of the catalyst suggests that the reaction proceeds via the *cis*-addition mechanism:



This results in the formation of PA with a *cis*-transoid structure. The formation of the *trans*-structure at high temperatures can be explained by the thermal isomerisation preceded by the crystallisation of the chains. An alternative possibility—the *trans*-dissociation of the triple bond in the catalytic complex—is sterically prohibited for the transition state;[35,36] the structure of the complex and the polymerisation kinetics have been examined in greatest detail elsewhere.[28,37]

In all the cases described above the synthesis results in the formation of fibrils[35] and the morphology of the PA films is almost independent of the conditions of synthesis. However, depending on these conditions, the diameter of the fibrils can vary from 200 to 10^4 Å and is usually 220–800 Å.[28,38] When the films are grown on supports, the size of the fibrils diminishes. The same effects have been observed in the synthesis of PA in other polymers. The size of the fibrils is particularly strongly affected by the time during which the catalyst is kept (its ageing); with increase in the ageing time, the size of the fibrils increases.[39] Detailed study of the growth of the fibril on thin films by transmission electron microscopy made it possible to observe microfibrillar branching on the main fibril (30 to 50 Å in size) and thickened regions at its entanglement sites as the presence of rings at the ends of the fibrils.

It has been shown that significant changes in the morphology of the film are not observed on isomerisation of PA. The film consists of arbitrarily arranged fibrils which are sometimes collected into larger formations.[36] The formation of the film is apparently a consequence of the interaction of the fibrils with one another via adhesion forces.

The synthesis of PA with fibrils oriented along some axis involves considerable difficulties. The simplest and most readily available method involves the stretching of the film, whereupon the fibrils are oriented predominantly along the stretching axis.[39] Crystalline specimens with a *trans*-structure, which give rise to a diffraction pattern similar to the Debye rings, are formed in the polymerisation of acetylene in a controlled shear field on a Teflon cylinder rotating at a rate of 3×10^3 rev min^{-1}.[40] It has been suggested that the polymer chain in these specimens is not oriented along the axis of the fibre. With increase in the rate of rotation of the cylinder, highly crystalline specimens are obtained in most axes of the fibril and the chains are parallel.[41] A method of preparation of macroscopic ribbon structures in a substrate rotating with a radial velocity of the mixing ring ranging from 10^7 to 10^{10} Å cm^{-1} [sic (Ed.of Translation)] which gives rise to the maximum shear stress in the future microfibrils has been described.[42] In the structures obtained, the molecular axis coincides with the axis of the fibre and the ribbon consists of a bunch of fibres. *trans*-Polyacetylene ribbons are more crystalline and the size of their domains is $(7-10) \times 10^5$ Å. A PA with a molecular weight of ~500, which can give rise to pseudo-lamellar structures, was found in the reaction medium.[42]

Oriented PA films are formed also on a polycrystalline Ziegler–Natta catalyst in solid biphenyl. The technique of deposition of the catalyst is fairly simple: on slow evaporation of the solvent from the mixture, a thin oriented layer of an active complex is produced on which a lustrous silvery PA film grows in the course of 3–5 days at −78 °C; the film is oriented in the direction of the single crystals of the support.[43]

Highly oriented PA films have been obtained by the polymerisation of acetylene which had been epitaxially oriented beforehand on the surface of crystalline benzene.[44] Oriented PA films have been synthesised on the basis of this idea using cyclohexylpropylalkoxybenzene in the liquid crystal state, in the presence of a Ziegler catalytic system at 18 °C.[45] Morphological studies have shown that the fibrils are almost fully oriented in the direction of the liquid crystal domains.[45] Anisotropic PA films have also been obtained by the polymerisation of acetylene in the nematic phase of the MBBA liquid crystal ($C_4H_9C_6H_4N-CHC_6H_4OCH_3$) in a magnetic field with a strength greater than 2500 G, but the orientation is insufficiently

pronounced.[45] Iodine-doped films having the composition $(CH)I_{0.15}$ exhibited appreciable anisotropic properties: their conductivity in the direction of the field was 1235 Ω^{-1} cm^{-1}, while at right angles to this direction it was 300 Ω^{-1} cm^{-1}.[46] X-Ray diffraction studies of the oriented films confirmed that their molecular and fibrillar axes coincide and that they have a high degree of crystallinity (~90%) and made it possible to explain features associated with the lattice parameters and the crystal system. The anisotropy of the electrical conductivity and of the optical properties of oriented films has been investigated in fair detail.[39]

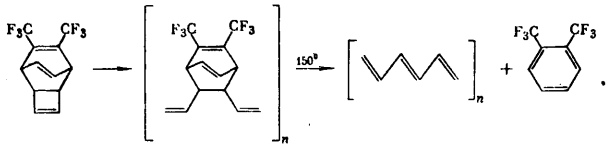
The metal complex catalytic systems are fairly varied. "Mixed systems", for example molybdenum or tungsten compounds combined with trialkylaluminium, have been used to an increasing extent in recent years for the preparation of various semiconducting polymeric materials. Lanthanide (Y, La, Pr, Gd, Tb, Dy) naphthenates or ethyl hexyl phosphates combined with triethylaluminium are effective catalysts of the stereospecific polymerisation of acetylene and its derivatives.[47] A catalyst component ratio of 1 : 5 is optimum. A polyacetylene obtained at a catalyst concentration ranging from 0.03 to 0.7 M at low temperatures contains 70% of the *cis*-isomer; according to the EPR data, there are 10^{17} paramagnetic centres per gram of the substance.[47] The results of X-ray diffraction studies (based on the characteristic $2\theta = 23.3°$ reflection), IR spectroscopic data and the initial conductivities of this specimen correspond to the values obtained for PA synthesised by other methods.[24-27] On the basis of such non-informative data, the not entirely justified conclusion has been reached[47] that the replacement of $Ti(OBu)_4$ by lanthanide compounds does not alter the PA structure.

The $AlR_3-VOCl(neopentyl)_2$ catalytic system is of great practical interest.[48] The PA obtained in its presence at -60 °C has a fibrous structure and can be processed by the usual method adopted in polymer technology. When a "mixed catalyst" is used, the particle size increases from 100 to 500 Å and the density of the film is found to increase. By filtering the suspension, it is possible to obtain a film of any size. Films on different supports, having effective adhesion properties, can be obtained by atomising the gel. The polymer can be readily doped with AsF_5, $FeCl_3$, I_2, and other electron acceptors; preliminary tests demonstrating certain advantages of such materials which are used in accumulators.[48] PA gels with analogous properties, obtained in the presence of other catalytic systems, are of great practical interest.[49] There is information in patent literature[50] about technological procedures for the preparation of PA films from gels with particle diameters in the range 0.01 – 1 mm, obtained in the presence of a "mixed catalyst" in the temperature range from -100° to -48°C. These results indicate the possibility of going over to a very simple and cheap technology involving a continuous process for the preparation of PA films.

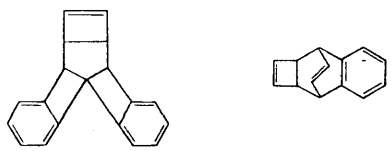
WCl_6 and $MoCl_5$, in the presence of which acetylene polymerises at 20 °C and pressures up to 14 atm, are comparatively readily available. However, the polymers obtained contain carbonyl groups, which is apparently due to the presence of oxygen, and have a low molecular weight.[51] Complex systems including tetraphenyltin in addition to WCl_6 or $MoCl_5$ are more promising for the preparation of film materials.[52] A PA film with a predominantly (to the extent of 90%) *trans*-structure and a "fibrous" morphology is formed on the surface of a concentrated solution of a vanadium catalyst. The diameter of the polymer fibrils, obtained in the presence of the $MoCl_5-Ph_4Sn$ catalyst can be varied in the range 300 – 10 000 Å; in the case of the WCl_6-Ph_4Sn catalyst, it reaches 1.2×10^5 Å.[30,52]

The study of the kinetics of the polymerisation of acetylene in the presence of $Ti(OBu)_4-Al(Et)_3$, WCl_6-Ph_4Sn, $MoCl_5-Ph_4Sn$, and $Ti(CH_2C_6H_5)_4$ catalysts showed that the rate of the process decreases in the above sequence.[31,52] Films doped with various acceptors, namely $(CHI_{0.25})_n$, $[CH(SbF_5)_{0.7}]_n$, and $[CH(CF_3SO_3H)_{0.18}]_n$, had a conductivity of 10 – 20 Ω^{-1} cm^{-1} at 20 °C.[53]

A new, novel method of synthesis of PA films in the *trans*-form involves the polymerisation of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]-deca-3,7,9-triene (BTFM) with opening of the ring:[54-55]



The polymerisation takes place in the presence of the $WCl_6-Sn(CH_3)_4$ catalytic system and deposits on the reactor surface. The prepolymer film splits off trifluoromethylbenzene with formation of a silvery PA film as a result of heating *in vacuo* at 100 – 150 °C. The density of the polymer reaches 1.1 g cm^{-3} and approaches the flotation density of the PA obtained by other methods. According to Leising et al.[54] and Edwards and Feast,[55] the amorphous PA obtained by this procedure has the fully *trans*-configuration and its structure is not fibrous. According to IR spectroscopic data, 1,2-bis-(trifluoromethylbenzene) residues are present in the polymer. Crystalline PA films with the monoclinic system and $\beta = 91.5°$ are obtained after prolonged heating of the prepolymer on electron microscope grids at 100 °C *in vacuo*.[56] An improvement of the method make it possible to obtain also films of fully oriented crystalline PA.[57] Subsequently methods of synthesis of polymers from other monomers were developed:[58]



On heat treatment of the prepolymer, naphthalene and anthracene are released in the former and latter case. An increase in the heat treatment temperature makes it possible to free the polymer from impurity residues.[58] According to spectroscopic data, the absorption due to the presence of sp^3-hybridised carbon is not observed in the spectra of the films; the absorption in the region of 1480 cm^{-1} in the Raman spectra of the polymers considered, due to the presence of C=C bonds, is displaced compared with the absorption observed for PA obtained by other methods (1460 cm^{-1}). It has been suggested that this is associated with a decrease in the size of the conjugation blocks. The films obtained are doped with difficulty in the gas phase owing to their high density. The conductivity of the initial films is 10^{-7} Ω^{-1} cm^{-1} and reaches 10 – 200 Ω^{-1} cm^{-1} when they are doped with bromine or iodine in solution and 2 Ω^{-1} cm^{-1} when the polymer having the composition $[CH(AsF_5)_{0.03}]_x$ is obtained.[58]

Solutions of ω-($\eta^1:\eta^5$-cyclopentadienyl)tris(η-cyclopentadienyl)-dititanium ($CpTiCl_2TiCp_2$) in hexane[59,60] and the cyclopentadienyl complex of sodium CpNa [61] exhibit a high catalytic activity. By removing the solvent slowly *in vacuo* from the PA gel formed, it is possible to obtain films with a metallic lustre. It has been suggested that the active complex has a tetrahedral structure and that the mechanism of the polymerisation is analogous to the mechanism of the polymerisation of olefins in the presence of a Ziegler – Natta catalyst.[61] The *cis*-polyacetylene films obtained at -80 °C had a conductivity of 240 Ω^{-1} cm^{-1} after doping.[60]

The classical ionic and radical polymerisation methods do not allow the preparation of high-molecular-weight polymers with a system of conjugated bonds (PCB) owing to the isomerisation of the active centres[2] associated with the polyene chain. With increase in the effective degree of conjugation, there is an appreciable change in electron affinity and the ionisation potential.[62] One of the methods

which make it possible to carry out the cationic polymerisation process involves the formation of a complex with the growing polyconjugated chain during synthesis. In practice such a process can be achieved in the presence of a large excess of a strong electron acceptor in the reaction medium. In this case, the electron density on polyene chains falls and there is a corresponding decrease in the probability of electron transfer from the chain to the active centre.

On the basis of these factors, it has been possible to synthesise PA films on the inner surface of the reactor in the temperature range from −78° to −198° when acetylene is added to arsenic pentafluoride. Soga et al.[63] and Kora and Kobayashi[64] identified the absorption band of *cis*-PA in the region of 740 cm^{-1} and of the doped complex in the region of 900 and 1370 cm^{-1}. Doped films having the composition $[CH(AsF_5)_{0.01}]_n$, obtained for the ratio $C_2H_2:AsF_5 \cong 0.1$, have an electrical conductivity of $4.8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.[63,64] Films of analogous composition have been obtained by the gas-phase polymerisation of vinylacetylene in the presence of SbF_5.[65,66] The conductivity of the film increased to $1 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ with increase in the SbF_5 concentration, but the metallic state could not be attained.

Soluble polyenes, including soluble PA, have been obtained in solution in AsF_3 in the presence of AsF_5 by cationic polymerisation,[67] which was carried out at the freezing point of acetylene; films having a conductivity of $10^{-6}-10^{-7}\ \Omega^{-1}\ cm^{-1}$, characteristic of weakly doped PA with a molecular weight of $\sim 10^{-3}$, could be cast from the solution obtained. Spectroscopic studies confirmed the presence of the *cis*-structure in the polymer obtained. The possibility, in principle, of the polymerisation of acetylenic monomers (acetylene, methylacetylene, cyanoacetylene, and perfluoroacetylene) with formation of high-molecular-weight products in the presence of Group III, IV, and V metal halides has been indicated.[64] Insoluble polymers with specific conductance of $10^{-3}\ \Omega^{-1}\ cm^{-1}$, obtained at −78 °C by polymerising acetylene in the presence of AsF_5, $NaAsF_5$, SiF_4, AsF_3, BF_3, SbF_5, and PF_6, are of practical interest.[68]

Bivalent mercury compounds or organomercury derivatives are effective cocatalysts of the cationic polymerisation of acetylene and its derivatives.[69] The reactions of mercury oxide or mercury salts with protic and aprotic acids in saturated hydrocarbon media result in the formation of heterogeneous complexes, which effectively polymerise acetylene, vinylacetylene, phenylacetylene, and propargyl alcohol. Polyacetylene mainly with the *trans*-structure and a degree of crystallinity of 70% has been obtained in the form of films in the polymerisation of acetylene on the catalyst surface.[62,69] According to X-ray diffraction data, the principal reflection corresponds to the interplanar spacing $d = 3.22$ Å.[62,69] A homogeneous catalyst, whose active complex with acetylene is stable at low temperatures, has been obtained in the presence of aromatic ligands.[69] In the presence of aromatic solvents (toluene, benzene), the solvent is alkylated and subsequently copolymerises with acetylene, as a result of which the IR spectra of the films show absorption bands corresponding to the aromatic ring. The characteristic features of the polymerisation of acetylenic monomers, the influence of temperature and catalyst composition on the structure, and the properties of the polymers obtained have been investigated.[70,71] A study of the morphology of the films demonstrated the absence of fibrils.

Virtually all the methods of synthesis enumerated above, which make it possible to obtain PA with a high molecular weight, lead to the formation of insoluble polymers. Their insolubility can be explained by the formation of network structures together with the intense intermolecular interaction. The degree of cross-linking of polymers obtained in the presence of Ziegler catalytic systems is 3−5% according to NMR data,[72] which has been confirmed by the results of ozonolysis.[73] Quantum-chemical calculations have confirmed that the isomerisation process results in the formation of intermolecular bonds leading to the appearance of an unpaired electron.[74]

The easiest and most promising method of synthesis of PA with a linear structure involves the polymerisation of acetylene in the presence of Group VIII metals in combination with reductants (Luttinger catalyst).[75-77] Polyacetylene with a high degree of crystallinity has been obtained by polymerising acetylene in the presence of the $Co(NO_3)_2-NaBH_4$ catalytic system with the 1 : 2 component ratio. In order to prevent the destruction of the catalyst, both components are introduced into the substrate containing the monomer. An increase in the temperature and sodium tetrahydroborate concentration leads to the partial reduction of the polymer. The activity of nickel complexes can be greatly increased if the polymerisation is carried out in the preence of $NaBH_4$.[62,77] A crystalline polymer obtained at low temperatures contains no fibrils; the crystallites have dimensions up to 70 Å. The characteristic reflection observed at $2\theta = 23.75°$ ($d = 3.74$ Å) confirms the *trans*-structure of the polymer. Palladium complexes are ineffective in the synthesis of high-molecular-weight polymers.[62,77,78] The Luttinger catalyst makes it possible to obtain linear polymers with the *cis*-structure distinguished by a high crystallinity. The yield of PA reaches 25−30 g per gram of catalyst.

The chlorination of freshly prepared polymers at low temperatures permits the synthesis of soluble chloropolymers with a molecular weight of $(2-5) \times 10^4$.[27,79] Although the authors claim that, in contrast to hydrogenation, at a low chlorination temperature the polymer did not undergo degradation, our data[80] indicate that, when the temperature and the solvent are selected appropriately, the chlorinated polymers obtained have a molecular weight up to 2.5×10^5; the degradation is more appreciable on chlorination in the light and at an elevated temperature. The linear structure of PA is demonstrated by the fact that soluble iodinated polymers are obtained by iodinating a suspension of PA in ethanol.[80]

Systematic study of the methods of synthesis of PA made it possible to develop a fairly simple and convenient method for the preparation of films on various supports wetted with an ethereal solution of the catalyst.[79] The disadvantages of these films as well as films obtained by Shirakawa's method[24,25] are the difficulties of freeing them from catalyst residues and the dependence of the properties on the thickness of the surface.[81] The methods for the preparation of PA films by atomising in an inert gas stream PA freed from catalyst residues or by casting homogenised gels are much more practical.[49,82,83] The properties of such films depend on the conditions governing their formation. "Free" films with a thickness up to 2−3 mm are obtained by the filtration under pressure in an inert medium of a homogenised suspension containing 5−10 g $litre^{-1}$ of PA formed in organic media at low temperatures in the presence of the $Co(NO_3)_2-NaBH_4$ catalyst. The films obtained by atomisation in an inert gas stream are homogeneous and exhibit an effective adhesion to metallic, polyurethane, polyester, poly(ethylene terephthalate), polyimide, etc. supports.

The properties of the films have been described as a function of the conditions of synthesis and the composition of the catalyst.[62,84] PA suspensions undergo an appreciable change in their properties in the course of time. In an inert medium at a temperature above −20 °C, cross-linking and aggregation of the fibrils are observed, which lowers the rate of oxidation and chlorination. The morphology of the films changes especially markedly when the suspension is aged in the presence of moisture and oxygen: the diameter of the fibrils increases, their length diminishes, and breaks and nodes are formed. In contrast to this, it has been claimed[85] that a PA suspension undergoes no changes in its properties on being kept for two weeks.

The preparation of soluble polymers with a stream of conjugated bonds and a large molecular weight is especially difficult owing to the strong intermolecular interaction, but a PA with a fairly high molecular weight has been obtained in the form of finely dispersed

particles by carrying out the synthesis in the presence of the Luttinger catalyst and surface-active substances, mainly copolymers of styrene and polyethylene with poly(ethylene oxide).[86] Acetylene was added at −60 °C to the catalyst and the copolymer in solution in the cyclohexane−tetrahydrofuran mixture and the mixture was heated to −30 °C. This resulted in the formation of stable colloidal solutions with spherical particles whose size ranged from 40 to 2000 Å; the density of the films isolated was 1.15 g cm^{-3}. Colloidal PA solutions can be obtained in the presence of other polymers which prevent the aggregation of the PA molecules produced.

Polyacetylene obtained in the presence of Group VIII metals combined with $NaBH_4$ possesses virtually the same morphology as the polymer synthesised by Shirakawa's method.[25] The dimensions of the fibrils are in the range 300−800 Å and depend on the catalyst concentration, the temperature of the synthesis, and the medium.[27,87]

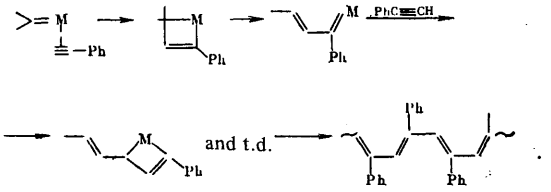
The thermogravimetric curves for the PA have two exothermic peaks at 145° and 325 °C.[16] The first corresponds to irreversible *cis*−*trans* isomerisation. At 325 °C hydrogen migrates, chain termination takes place, and the PA is cross-linked without the formation of volatile products; the polymer acquires a brown colour and a large number of defects appear, which is reflected in the appearance in the IR spectra of absorption bands characteristic of CH_2, CH_3, −C=C−, and C_6H_5 groups.[16] It has been suggested that structure formation takes place in the polymer in the temperature range 280−380 °C. The exothermic peaks in the region of 425° and 440 °C correspond to the partial decomposition of the PA; 72% of the initial mass of the PA is lost at 720 °C. The main products of the decomposition of the PA are benzene, hydrogen, and lower hydrocarbons.[15] When PA is heated in air to 90 °C, the degree of its crystallinity falls after only a few hours and a brown amorphous substance resembling cuprene is obtained when 70 h have elapsed.

III. THE SYNTHESIS AND PROPERTIES OF POLYACETYLENE DERIVATIVES

The likely usefulness of PA for the preparation of electrodes in accumulators and new semiconducting materials for the electronic industry stimulated further search for further technological materials. One of the ways in which such search is prosecuted involves the study of the polymerisation of acetylene derivatives and of the properties of the material formed.

The golden-green amorphous films of poly(hepta-1,6-diyne), obtained by the polymerisation of the corresponding monomer in the presence of a Ziegler−Natta catalyst, have the most interesting electrophysical characteristics.[88] In addition to the absorption in the region of 1610 cm^{-1}, characteristic of polyenes, the IR spectrum of this polymer exhibits absorption in the region of 910 and 1430 cm^{-1}, indicating the presence of the methylene group. A cyclic structure has been proposed for the polymer on the basis of these data. The conductivity of the freshly prepared specimens is 10^{-12} Ω^{-1} cm^{-1} and reaches 10 Ω^{-1} cm^{-1} when they are doped with AsF_5. The undoped films have a density of ~1 g cm^{-3}. A transition of the polymer to the vitreous state has been observed by differential scanning calorimetry in the temperature range from −50° to 330 °C; the first exothermic peak, associated with the *cis*−*trans* transition, is observed at 127 °C and the second occurs at 267 °C. The poly(hepta-1,6-diyne) films differ from the polyacetylene films by the fact that they contain no fibrils and are more sensitive to oxygen.[88]

One of the most readily available acetylene derivatives is phenylacetylene (PhA). The method for its polymerisation and the properties of polyphenylacetylene (PPhA) have been studied in fair detail and have been described[12,16,89,90] and we shall therefore consider only certain questions concerning the preparation of semiconducting materials from PhA. The polymerisation of PhA in the presence of $AlEt_3-TiCl_4$ leads to the *cis*-isomer [91] or the *trans*-isomer [92] depending on the conditions of synthesis; the pure *cis*-cisoid PPhA has a bright red colour. The crystalline insoluble *cis*-PPhA is obtained in the presence of iron acetylacetonate and trialkylaluminium.[91] The soluble *cis*-PPhA with $M_n = (1-2) \times 10^4$ is formed in the presence of $MoCl_5$ or WCl_6.[93,94] The kinetics of the polymerisation of PhA in the presence of $MoCl_5$ catalyst fixed on kaolin, talc, and aluminium and magnesium oxides have been investigated[95] and it was found that the carrier influences the structure and properties of PPhA. The molybdenum in the active centre exists in the quadrivalent state.[95] High-molecular-weight PPhA with $M_n \cong 8 \times 10^4$ has been obtained in the form of a yellow soluble powder on UV-initiated polymerisation of the monomer in the presence of tungsten or molybdenum carbonyl in a halogen-containing solvent.[96] It has been suggested that the reaction mechanism involves the elimination of carbon monoxide under the influence of UV irradiation with formation of a coordination complex between the carbonyls of the above metals and PhA. The polymer chain grows in the consecutive stages involving the formation of the metallocarbenes and metallocyclobutenes:



The films can be readily obtained from the polymer solutions.

Although the electron-initiated polymerisation of arylacetylenes is in fact fairly promising, it has been little investigated.[97,98] The PhA polymers obtained in dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and acetonitrile in the presence of tetra-alkylammonium, lithium, potassium, and sodium salts or $NaNO_3$ as electrolytes have a low molecular weight (of the order of 500−3700) and a melting point ranging from 90° to 160 °C. The synthesis takes place in the cathodic space on graphite electrodes; the radical inhibitors do not influence the polymerisation but alcohols retard the process. On the basis of these data, the authors propose an ionic initiation mechanism. The yield of the polymer, in which a large amount of cyclohexadiene structures has been observed, reaches 60%.[97-100]

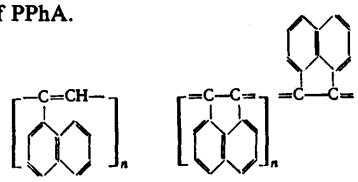
The PhA polymerises in a homogeneous catalytic system consisting of mercury compounds combined with acids in aprotic solvents.[101] The soluble polymers formed, mainly with the cisoid structure, are distinguished by a high degree of crystallinity. The films obtained from the solution of the polymer weakly doped with boron trifluoride exhibit semiconducting properties and have an electrical conductivity of the order of $10^{-6}-10^{-8}$ Ω^{-1} cm^{-1}; they lose their crystallinity on ageing. It follows from the analysis of the IR and ^1H NMR spectra that, under these conditions, cyclohexa-1,3-diene and cyclohexa-1,4-diene structures, diminishing the effective conjugation, appear in the polymers.[101,102] The stable complexes of PPhA with iodine, which are formed when PhA is polymerised at 100° to 150 °C in the presence of iodine as the catalyst, have an electrical conductivity of the order of $10^{-3}-10^{-5}$ Ω^{-1} cm^{-1}.[103]

The appeciable defects in the conjugation chain in PPhA compared with PA are caused not only by the influence of the benzene ring, which gives rise to steric hindrance to the coplanarity of the fragment of the main chain, but also by the tendency of the PPhA to isomerise. The isomerisation takes place at temperatures up to 130 °C and is accompanied by a slight decrease in the molecular weight; analogous changes have been observed to a large extent after the specimens have been kept for a long time in the light.[104,105] An appreciable decrease in $\overline{M}_n$ and the appearance of cyclohexadiene

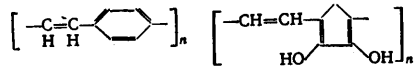
fragments have been observed at 130–280 °C.[106] Further heating leads to weight loss, which is associated with the evaporation of the low-molecular-weight products—mainly triphenylbenzene.[107] These changes result in the complication of the polymer structure, a decrease in the length of the effective conjugation, and hence an impairment of the electrical conductivity.[99] For example, the electrical conductivity of the iodine-doped crystalline *cis*-cisoid PPhA falls by several orders of magnitude after its heat treatment at 120 °C. Apparently this is why a dependence of the electrical conductivity of PPhA on its structure and molecular weight has not been observed in many investigations. On doping with iodine, the electrical conductivity of PPhA reaches 10^{-5} Ω^{-1} cm^{-1}, the *cis*-isomer being doped more readily than the *trans*-isomer. Variation of the molecular weight over the range $(7-10) \times 10^3$ does not affect the reversible incorporation of iodine and the conductivity of PPhA.

Soluble complexes of PPhA with organic electron acceptors have been obtained; their solutions absorb radiation in the range 700 to 900 mm as a function of the nature of the electron acceptor.[108] The electrical conductivity of the polymer increases after the addition of the acceptor, reaching a maximum when the content of the latter is 75 mole per cent and does not then change further. Analogous behaviour has been observed also for polystyrene.[108] The authors suggest that the acceptor forms a complex with the phenyl side groups in the polymer chain. However, a study of the kinetics of the reaction of PPhA with chloroanil and other organic acceptors demonstrated the formation of a charge-transfer complex (CTC) in the first stage of the process and the subsequent complete charge transfer with formation of a polymeric radical-cation.[109] The equilibrium constants for the complex ($K \geqslant 10^3$) have been estimated and its enthalpies have been found ($\triangle H \geqslant 8.6$ kcal $mole^{-1}$) from the activation energies ($E_{eff} = -8.6$ kcal mol^{-1}). Further studies showed that styrene does not form a CTC with iodine.[110]

Methods for the polymerisation of 1-ethynylnaphthalene[89,111] and acenaphthenediylidenes with various substituents[112] have also been investigated. The electrophysical properties of the polymers obtained have been described in fair detail[111,112] and are in the main similar to the properties of PPhA.



Polyarylacetylenes capable of forming films with metallic lustre and having a specific conductance (for undoped specimens) of 10^{-8} Ω^{-1} cm^{-1} each and having the following structure have been obtained by photoreductive condensation:[113]



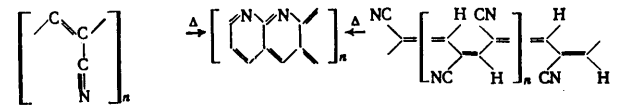
The synthesis, structures, and properties of polyarylacetylenes have been described in great detail in a review.[90]

Among other polymeric derivatives of acetylenes, poly(3,3,3-trifluoroprop-1-yne) is of interest. Trifluoromethylpropyne is polymerised in solution in DMF in the presence of $PdCl_2$ at 60 °C.[114] Liquid oligomers, which have a polyene structure according to IR and NMR spectroscopic data, are formed. A higher-molecular-weight product with $M_n \cong 10^3$ was obtained at −78 °C in the presence of butyl-lithium.[78] On heat treatment, the brown polymer powder blackens, but its conductivity $\sigma = 10^{-12}$ Ω^{-1} cm^{-1} does not change; specimens doped with iodine have a conductivity of 9.5×10^{-5} Ω^{-1} cm^{-1}. The polymer is resistant to thermal and thermo-oxidative degradation up to 240 °C. In the differential-thermal analysis of the specimen in the temperature range up to 450 °C, three exothermic peaks are observed.[78,114]

A polymer with a conductivity up to 10^{-5} Ω^{-1} cm^{-1}, described previously,[115] has been obtained by the polymerisation of propargyl chloride in the presence of $PdCl_2$.[114] The high conductivity is apparently due to the doping of the polymer by the halogen eliminated. The introduction of an excess of iodine into the polymer powder softens it and a thin film with a conductivity of 2×10^3 Ω^{-1} cm^{-1} can be obtained from it by pressing.

Like cyanoacetylene, propiolonitrile readily polymerises in the presence of various catalysts.[116] In the presence of triethylamine, a black insoluble powder is formed in high yields; in order to obtain films, the reaction is carried out in the gas phase. The BuLi catalyst in THF polymerises cyanoacetylene at −70 °C ($\overline{M}_n \cong 4800$). The effective adhesive properties of the films make it possible to grow them even on the surface of Telfon; splitting into layers on deformation of the support is not observed.[114,117,118] In the presence of $Ti(OBu)_4-AlEt_3$, the reaction involving the formation of a *cis*-transoid polymer takes place in solution in pentane at room temperature but the yield of the polymer is somewhat lower than in the presence of chromium acetylacetonate with an excess of triethylaluminium.[116] A brown polymer with a linear *trans*-transoid structure can also be obtained.

Catalysts based on $MoCl_5$ and $Sn(C_6H_5)_4$ make it possible to obtain linear products from cyanoacetylene at room temperature.[116] The polymer is not doped by electron donors but it is reversibly doped with iodine up to a content of the latter of 40 mole per cent. Its electrical conductivity then changes from 10^{-12} to 10^{-3} Ω^{-1} cm^{-1}. Differential-thermal analysis data indicate the occurrence of processes at 140°, 215°, and 255°C without change in rate. The weight loss at 1110 °C is ~50%. The study of the specimens after the heat treatment suggested that the first stage (280 °C) involves isomerisation, while at higher temperatures cyclic structures appear as a consequence of degradative processes:[114]



linear *trans*-transoid polymer

linear *cis*-transoid polymer

The cyanoacetylene polymers and copolymers exhibit semiconducting properties and are promising materials for the preparation of transistors and solar batteries.[117,118]

Polymethylacetylene has been obtained[119] by the polymerisation of methylacetylene in the presence of a Ziegler–Natta catalyst at 0 °C. The orange powder obtained is sensitive to air and does not give rise to an EPR signal even on heating to 150 °C. The results of thermogravimetric analysis indicate its vigorous decomposition at 180 °C with a weight loss of up to 90%.[119] Polymethylacetylene is doped with iodine and other electron acceptors whereupon $\sigma = 10^{-3}$ Ω^{-1} cm^{-1} is attained. The films are formed on gas-phase polymerisation of methylacetylene on the surface of the catalyst at low temperatures. The polymerisation of ethynylferrocene and methylethynylferrocene takes place readily in the presence of WCl_6-Ph_4Sn.[120]

Other acetylene derivatives containing bulky substituents, capable of fully disturbing the coplanarity of the chain, as a rule polymers with poor electrophysical properties. For example, the polymerisation of t-butyl- or n-butyl-acetylene under the influence of WCl_6 leads to the formation of light-coloured powdered products with $M_n \cong (0.8-5) \times 10^5$ which do not possess the properties of PCB.[121] Table 1 indicates certain acetylenic derivatives used as monomers for the synthesis of PSS.

IV. COPOLYMERS AND COMPOSITES BASED ON POLYACETYLENE

The search for methods of synthesis of polyenes is closely related to the modification of the properties of these polymers in order to obtain materials which are suitable for processing on the technological equipment used in the polymer industry. One of such current procedures is the preparation of copolymers of acetylene and its derivatives with other monomers used in industry and composites. Films containing 2–5% of DA, capable of being doped with electron-acceptors, have been obtained by polymerising acetylene in a matrix comprising polyethylene and copolymers of styrene with butadiene and isoprene using a Ziegler–Natta catalyst.[122,123] The dispersed doped compositions have a high surface conductivity and an improved resistance to the action of air. The number-average molecular weight of the PA composition reaches 2.5×10^4, while the weight-average molecular weight M_w is 10^5, so that we have the ratio $M_w/M_n = 4.26$.[124] The properties of the conducting composites obtained by doping the polymer with iodine and having a PA content up to 3% can be explained by a simple percolation model.[125]

Flexible elastic films can be obtained by pressing PA with ethylene–propene rubbers or by polymerising acetylene in solution in poly(vinyl chloride), polyvinylpyrrolidinone, or polyvinylbutyral; the stretching of the films promotes an increase in electrical conductivity, which can be explained by the orientation effect.[126] The most varied materials, ranging from elastic to rigid, can be obtained by polymerising acetylene in the presence of the $Ti(OBu)_4-AlR_3$ catalyst in a polybutadiene matrix with $\overline{M}_n = 2 \times 10^5$. When they were doped with lithium or iodine, a composite having a conductivity ranging from 10 to 100 Ω^{-1} cm^{-1} was obtained; the conductivity increases on stretching the specimens.[127] The morphology of the composites varies as a function of the PA content from fibrillar (for an 80% PA content) to globular (PA content less than 20%).[128] Electrically conducting compositions have been obtained by the graft polymerisation of acetylene. The addition of PA to the copolymer chain has been demonstrated.[123] The graft block-copolymer of PA and atactic polystyrene with $M_n = 10^5$, obtained in the presence of a Ziegler–Natta catalyst and containing up to 40% of PA, is capable of forming lamellar single crystals which have a hexagonal lattice whose unit cell parameters are $a = 5.12$ Å and $c = 4.8$ Å and whose size ranges from 10^3 to 10^4 Å.[129] With decreased content of the polymer-carrier, the interface necessary for the formation of the crystalline phase diminishes.

A soluble block-copolymer of PA with polyisoprene and polystyrene is obtained for a PA content up to 5% and permits the study of the behaviour of the stable PA chain in solution. Spectroscopic studies[130] have shown that in such copolymers the polyene molecule retains the properties of the homopolymer. However, there are also certain differences. Thus at room temperature rapid *cis–trans* isomerisation takes place in the copolymer. The block-copolymer is more sensitive to oxidation than PA itself and, in contrast to PA or the composite, it is capable of combining quantitatively with bromine at the double bond. NMR data have made it possible to identify segments with PA and to establish that the chain conformation is non-linear. According to electron microscopic data, the graft copolymers are characterised by the presence of separate microphases with microdomains $(1-1.5) \times 10^5$ Å in diameter.[130,131]

The PA and styrene block-copolymers have been obtained from styrene oligomers with $M_n = 10^3$ synthesised in the presence of BuLi. After the treatment of the oligomer with aluminium chloride and the addition of $Ti(OBu)_4$, acetylene was introduced into the system at a pressure of 700 mmHg. This method makes it possible to obtain also copolymers of acetylene with methylacetylene and phenylacetylene.[37] The films made of copolymers with different contents of methylacetylene have also been obtained by polymerising a mixture of monomers on a thin layer of catalyst deposited on a support.[119] The elasticity of the polymer increases with increase in the methylacetylene content whereupon the conductivity of the doped film and its stability in air diminish. With increase in the methylacetylene content in the copolymer, its morphology changes appreciably and the fibrillar structures characteristic of PA disappear.[119]

The reverse process involving the grafting of polystyrene, polyisoprene, poly(methyl methacrylate), and poly(ethylene oxide) blocks to the PA chain is carried out by polymerising the corresponding monomers on polyacetylene doped with sodionaphthalene. Films

Table 1. The polymerisation conditions and the properties of the acetylenic polymers.

Initial monomer	Polymerisation catalyst	Conductivity, Ω^{-1} cm^{-1}		Refs.
$CH_2{=}CH$	$Ti(OBu)_4$—AlR_3	10^{-13}—10^{-9}	(film)	[114, 119]
$CH_3C{\equiv}CH$	BuLi	10^{-13}—10^{-5}	(powder)	[78, 114]
$ClCH_2$—C≡CH	$PdCl_2$-pyridine	10^{-4}—10^{-3}	(powder)	[114, 115]
HO—CH_2—C≡CH	Hg^{2+}-acid, KOH, $PdCl_2$	10^{-10}—10^{-8}	(powder)	[62]
$CH_2{=}CH$—C≡CH	SbF_5	10^{-2}	(film)	[65, 66]
C_3H_7—C≡CH	NiX_2 — $NaBH_4$	—	(powder)	[75]
C_4H_9—C≡CH	WCl_6, $Ti(OBu)_4$ — AlR_3	$>10^{-14}$	(film)	[121]
NC—C≡CH	$A^-(NR_3$, BuLi) *	10^{-6}—10^{-3}	(film)	[117, 118]
NC—C≡C—CN	$Ti(OBu)_4$ — $AlEt_3$	10^{-6}	(film)	[116]
C_6H_5—C≡CH	$MoCl_5$, WCl_6, SbF_5	10^{-5}	(film)	[66, 89, 94, 114]
C_6H_5—C≡C—C_6H_5	electrochemical method	—	(powder)	[97]
$C_{10}H_7$—C≡CH	BuLi	10^{-7}	ilm, powder)	[65, 66, 89, 111]
HC≡C—$(CH_2)_3$—C≡CH	$Ti(OBu)_4$ — AlR_3	10^{-13}—10^{-1}	ilm)	[88]
R—OOC—C=CH(R=CH_3, C_6H_5)	electrochemical method	—	(powder)	[97]

*Here A^- = anion.

with interesting magnetic properties have been obtained by copolymerising acetylene with carbon monoxide.[131] An amorphous polymer containing up to 15 mole per cent of CO and having molecular weights up to 87×10^4 can be synthesised in the presence of the $Ti(OBu)_4-4AlEt_3$ catalyst. The AsF_5-doped films had conductivities up to 200 Ω^{-1} cm^{-1}.[131] When epoxyethane is used, materials having the properties of solid electrolytes are obtained.[37] In recent years, there has been a marked growth of interest by investigators in composites containing PA. Composites containing graphite, carbon black, charcoals,[132] various network polymers, and, in particular, thermolysed polyacrylonitrile[48] have been produced. Composites obtained by polymerising acetylene on polypyrrole films are of interest; after doping, they have a conductivity of ~ 20 Ω^{-1} cm^{-1} and are fairly stable in air.[133]

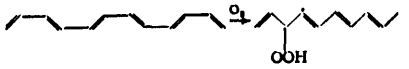
V. THE OXIDATION, REDUCTION, DOPING, AND STABILISATION OF THE FILMS

The ability of PA and other PCB to combine with 25–33 wt.% of oxygen in air is evidence of their instability, although the use of this property for special purposes can be of independent practical value. The oxidation of PA alters the chemical and physical characteristics of the material. The electrophysical and mechanical properties of films change particularly markedly.[134] On absorption of oxygen, the material becomes more brittle; the slight modification of the surface of the fibrils in consequence of the adsorption of oxygen or other acceptors greatly influences the formation of films. The films doped with acceptors are oxidised more slowly than the initial films.[135,136] The electrical conductivity of PA films increases after the absorption of oxygen up to 16 wt.% and then falls by several orders of magnitude.

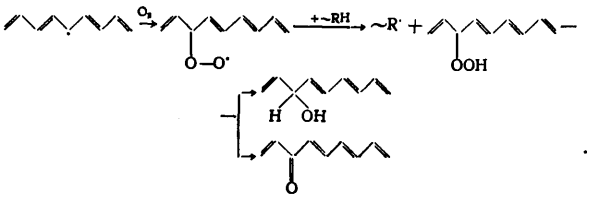
The absorption bands of the oxidised specimens in the region of 1720 and 1670 cm^{-1} correspond to the deformation vibrations of the carbonyl group in the isolated and αβ-unsaturated ketones.[138] Bands at 1109 and 1143 cm^{-1} correspond to the antisymmetric vibrations of the C–O bond in aliphatic ethers. The absorption bands in the range 1000–1300 cm^{-1} and in the region of 3420 cm^{-1} indicate the appearance of hydroperoxy- and hydroxy-groups. The absorption bands at 1370 and 890–900 cm^{-1} appear in the initial stage of the oxidation caused by the doping of the PA with atmospheric oxygen and disappear at high degrees of oxidation; the absorption in the region of 1920 cm^{-1}, attributed to the allene group, vanishes simultaneously.[136-139]

There exist several ways of adding oxygen to polyenes. Singlet oxygen can react with the olefin via the 1,2-addition mechanism with the ultimate formation of cyclic peroxides. In the case of 1,3- and 1,4-addition, other corresponding products appear. Triplet oxygen reacts with the initial radical to form a peroxy-radical capable of being converted into hydroperoxy-, carbonyl-, and hydroxy-groups as a result of further reactions.[136] The oxidation occurring in the absence of UV irradiation is a pseudofirst order reaction.

Visible light does not affect the rate of oxidation; diffusion also does not limit the rate of the process. In the oxidation of the films, an induction period, corresponding to the formation of a CTC, is observed; this is followed by two oxidative processes on the surface and in the bulk of the specimen, which lead to the appearance of an inflection in the kinetic curve. The following reaction scheme has been proposed on the basis of the studies carried out:[136,140]



The oxidation of *cis*-PA begins with the isomerisation and formation of neutral defects:



However, the scheme presented reflects inadequately the specific features of the oxidation process in view of the complex character of the reactions of oxygen with the polyconjugated system. The results of the study of the kinetics of the oxidation of PA indicate the absence of a linear relation between the decrease in the number of double bonds and the accumulation of oxidised groups.[138] The kinetics and mehcanism of the oxidation of PA have been described in detail in other communications.[30,141]

Owing to the preferential consumption of molecules with a *cis*-structure, in the initial stage of the oxidation of PA, the enrichment of the specimen in the *trans*-isomer is observed. If the temperature does not exceed 150 °C, the oxygen content of the polymer can reach 35%. With increase in temperature, thermo-oxidative degradation, in the course of which CO_2 and H_2O are evolved, takes place.[136,138] The rates of oxidation at 70 °C of PA and polymethylacetylene obtained in the presence of a Ziegler–Natta system are respectively 9.16×10^{-7} and 10^{-6} mol g^{-1} s^{-1}, while the activation energies for these processes are 9.6 and 14 kcal mol^{-1}.[142] The activation energies for the oxidation of PA measured by different workers are in the range from 11 to 20 kcal mol^{-1},[136,139,143] which is apparently associated with the different densities of the films employed. The activation energies for the formation of the complex of PA with oxygen and for its decomposition have been found respectively to be 11.52 and 13.45 kcal $mole^{-1}$ and it has been shown that water accelerates the oxidation of PA.

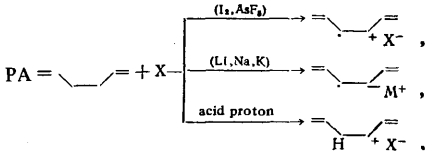
The addition of ozone to polyenes takes place at low temperatures and leads in the case of PA to the formation of an adduct in 98.5% to 99.5% yields whose decomposition results in the formation of oxalic acid diesters.[73] The activation energy for the oxidation of PA by ozone is 19.59 kcal mol^{-1}.[144] The kinetics of the oxidation and doping of polyheptadiene and PA differ somewhat.[145]

Studies of different types of stabiliser have shown that quenching agents for singlet oxygen, for example, dimethylanthracene as well as compounds decomposing peroxides do not affect the rate of oxidation of PA.[142] Sterically hindered phenols and inhibitors of the amine type, which actively capture radicals, inhibit the thermal oxidation of PA. The inhibition of the oxidation of PA also occurs on the addition of mixtures of sterically hindered phenols and peroxide-decomposing compounds which exhibit a synergistic effect. Following an increase in temperature the action of antioxidants weakens; this is believed to be caused by the surface character of the inhibition.[142] In the presence of 2,6-di-t-butylphenol, the stability of PA is retained also after doping. The kinetics of the oxidation of PA have been studied in the presence of inhibitors.[30,136] Analogous results have been obtained in the study of polymethylacetylene synthesised in the presence of a Ziegler–Natta catalyst; stabilisers of the phenolic type are effective if they are used in a complex with systems decomposing peroxides.[146]

The stability of various polymers of the acetylene series in relation to oxidation in air and UV irradiation increases in the presence of acid esters and thioesters based on Group V and VI elements, especially phosphorus, sulphur, nitrogen, etc.[141] A polyacetylene synthesised in the presence of phenols and phosphines is also less susceptible to oxidation. It is likewise resistant to the action of water, but its doped derivatives, especially those doped with electron

donors, are sensitive to moisture. The PA doped with sodium is readily hydrolysed by water, whereupon its partial hydrogenation takes place.[147] The elecrical conductivity of the films doped with electron acceptors falls in the presence of moisture owing to the hydroxylation of the PA, particularly in alkaline media. Chain protonation takes place in acid media and the stability of the films is higher than in an alkaline medium.[148,149] In strongly acid HBF_4 solutions, it is possible to dope PA irreversibly without the formation of hydroxylation products.[150,151]

Doping of *p*-type includes in essence a PA oxidation step and occurs fairly vigorously with the cooperation of various acceptors. Correspondingly, *n*-type doping includes a reduction process and occurs with the cooperation of electron donors. In early studies, the doping mechanism in the first stage was described by the scheme[36]



Here provision is made for the delocalisation of the cations and anions formed along the conjugation chain. Later this scheme was confirmed by the finding that, following the addition of external oxidants, the rate and degree of doping increase and hydroxy-groups can be detected in the PA structure.[152] As already mentioned, the ability of PA to be doped with an electron acceptor or donor is its most important characteristic, which makes it possible to employ this material as *n*- and *p*-type semiconductors, electrodes, solar energy converters, in the manufacture of accumulators, and in other technological fields. In the vertical stage of the reaction with PA, oxygen acts as an electron acceptor, which entails an increase in the conductivity and the appearance of an interfacial polarisation effect.[139]

One of the most promising methods of doping is electrochemical. The irreversibility of electrochemical doping, investigated in a number of studies,[153,154] made it possible to develop doped polyacetylene electrodes for accumulators.[155,156] In a general form, the equation for the doping process can be written as follows:

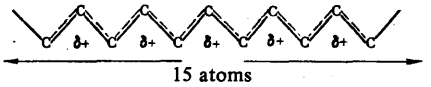
$$CH_x + yA \rightarrow [CH^{y+}(A^-)_y]_x ,$$

$$CH_x + yM \rightarrow [M_y^+(CH)^{y-}]_x ,$$

where A^- and M^+ are the univalent anion and cation respectively.

As in the oxidation reaction, a *cis*–*trans* transition is observed in the PA during the doping process and, depending on the degree of doping, three states of PA arise. In the first, semiconducting state, the concentration of the dopant is less than 1% and the material has semiconducting properties. In the second, metallic state, where the concentration of the dopant exceeds 6%, the material acquires properties characteristic of metals: high conductivity independent of temperature, paramagnetic susceptibility, and low heat capacity; its thermo-e.m.f. begins to vary linearly with temperature, etc. Finally, in the transition state, the material occupies an intermediate position between metals and semiconductors as regards its properties.

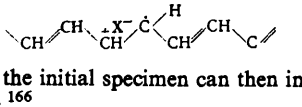
At the present time, the high conductivity of doped PA is explained mainly by the mobility of solitons. Neutral solitons, called in the chemical literature "delocalised radicals",[157] exhibit a high mobility in *trans*-PA. Positive and negative solitons (carbonium ions and carbanions) appear as a result of electron transfer to an acceptor (*p*-doping) or from a donor to the polymer (*n*-doping). The unit charge of the solitons is distributed approximately between 15 carbon atoms:



The charge on each CH group diminishes with increase in its distance from the doping ion.[158] Analysis of the IR spectra provides proof of the appearance of solitons. The vibrational models of soliton are observed at 1385 and 900 cm^{-1}, which is consistent with calculated data.[9,105] However, the properties of PA in the initial doping stage can be accounted for differently, with the aid of the theory of the formation of polarons.[159]

The general characteristics of the doping by various electron acceptors are the same. X-Ray diffraction studies on the iodine-doped PA indicate the existence of undoped regions and regions doped on the surface; furthermore, there are also complexes of PA with the dopant exhibiting metallic conductivity.[160] It has been observed by NMR that, together with complex formation, iodine adds to the double bond.[161] The doping of PA films obtained using the $Co(NO_3)_2-NaBH_4$ catalytic system is achieved both by immersing them in solutions of different acceptors and electrochemically until the attainment of a conductivity $\sigma \cong 10^3\ \Omega^{-1}\ cm^{-1}$.[162] In the doping process, the characteristic reflection of *cis*-PA with $d = 3.73$ Å disappears and reflections with $d = 8.35$ Å appear when SbF_5 is used as the dopant and $d = 8.15$ Å when AsF_5 is used; similar reflections have been noted for doped graphite ($d = 8.46$ and 8.15 Å respectively). A layered structure has been proposed for the doped specimens on the basis of these investigations.[162] When the PA film is doped with fluorosulphonic acid in the gas phase, the conductivity increases rapidly with increase in the content of the dopant y up to the critical value $y = 0.02$, after which a tendency towards saturation is observed, occurring at $y = 0.29$, whereupon σ reaches $2 \times 10^4\ \Omega^{-1}\ cm^{-1}$. At low temperatures the conductivity is independent of temperature, which can be explained by the vibrationally-excited tunnelling of the charges between the metal-like sections.[163] Detailed investigation of the doping of PA films indicate a non-uniform occurrence of this process, because the diffusion of the dopant into the relatively dense fibrils is difficult.[164]

A novel doping method involves the implantation of halogens in PA. Treatment of PA with a stream of halide ions at a dose of $10^{11}-10^{17}$ ions cm^{-2} and for an irradiation energy of 10–40 eV generates a uniform ion concentration gradient along the specimen. This film then becomes stable in air and acquires a colour ranging from red to blue depending on the irradiation energy. It has been suggested[165] that complexes having the following structure are formed in the ion implantation process:



The conductivity of the initial specimen can then increase by five orders of magnitude.[166]

The doping of PA by acids, especially those which cannot behave as oxidants is of special interest. The addition of a proton to the polyene chain with formation of a complex is suggested in this case.[167] The doped polymers have a comparatively low electrical conductivity (up to $10^{-3}\ \Omega^{-1}\ cm^{-1}$). This has been explained[167] by the appearance of steric effects, the formation of cross-links, or the addition of HCl to the double bond, which limits the length of the conjugation chain.[168] However, this evidence was in no way confirmed in the above study; furthermore, we have shown† that the addition of HCl to the double bond is not observed.

Doping with alkali metals can be carried out most readily in solution in tetrahydrofuran using sodium naphthalide or benzophenonelithium as the dopant; as in the *p*-doping process, under these conditions absorption bands in the regions of 1090 and 1480 cm^{-1}, characteristic of the *trans*-isomers, appear in the Raman

† See A.A.Matnishyan, N.M.Davtyan, and G.R.Martirosyan, Vysokomol.Soed., 1987, **29B**, 728.

spectra of *cis*-PA.[169] Doping with lithium tetrahydroaluminate in solution leads to the formation of a relatively unstable PA anion with a conductivity of 5 Ω^{-1} cm^{-1}.[170,171] In order to prepare elastic *n*-type films, PA is treated with anthraquinone derivatives combined with reductants (KBH_4, $NaHSO_3$, $NaCNBH_3$) in an aqueous medium.[172] Although the stability of the films increases in such treatment, nevertheless doping is accompanied by the partial reduction of the polymer and hence by the destruction of the conjugation regions. PA films treated with biarylyliodonium salts, whose UV irradiation leads to the doping of the exposed sections accompanied by an increase in conductivity, have found a new practical application as photo-sensitive materials.[173] The characteristic features and mechanisms of the doping of PA have been investigated in fair detail in recent years in connection with the prospect of constructing accumulators using PA films as electrodes.

Phenylacetylene is irreversibly doped with iodine, whereupon its conductivity increases from 10^{-14} to 10^{-5} Ω^{-1} cm^{-1}. The dependence of the conductivity on the iodine concentration c is of the form[159]

$$\sigma = \sigma_0 \cdot \exp[\gamma c(1-c) - \gamma/4],$$

where $\gamma \cong E/kT$.[159] An ionic mechanism of electrical conduction involving the thermally activated charge transfer model has been proposed. The current is determined by the number of charge carriers and not by their mobility.[114,174] Complexes of PPhA with various organic and inorganic acceptors were obtained. A mixture of PPhA with dichlorodicyano-*p*-benzoquinone and tetracyano-*p*-quinodimethane exhibits a high conductivity and measurements of the thermo-e.m.f. made it possible to assign it to the *n*-type.[108]

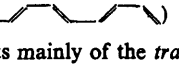
Among other polyenes, doped polyheptadiyne, polymethylacetylene, and certain polyarylacetylenes have been investigated.[112]

VI. THE STRUCTURE AND MORPHOLOGY OF POLYENES

Studies of PA films obtained both in the presence of Ziegler–Natta catalysts and Group VIII metals led to the conclusion that the *cis*-form of the polymers includes the *cis*-transoid structure



and the *trans*-cisoid structure



while the *trans*-form consists mainly of the *trans*-transoid structure[16,27]



The formation of the *cis*-cisoid structure is not ruled out either. The content of the *cis*-form in the synthesis of the polymer on the support or on the catalyst surface depends on the thickness of the film; as a consequence of the appreciable heat of reaction observed when the films are obtained by the method of Shirakawa and co-workers,[24,25] the fraction of the *cis*-isomers in thick specimens falls to 70–75% owing to their transition to the *trans*-form.[174] However, since the activation energy for the isomerisation reaction increases rapidly as the *trans*-structures accumulate and reaches 21 and 38 kcal $mole^{-1}$ for contents of the *cis*-form of 70 and 20% respectively, this explanation cannot be regarded as exhaustive.[143] If the polymerisation is carried out in the presence of the $Co(NO_3)_2$–$NaBH_4$ catalyst, the *trans*-cisoid structure is formed in appreciable amounts on the supports together with the dominant *cis*-transoid structure;[175] the fraction of the *cis*-cisoid structure is negligible. The ratio of the isomers depends greatly on the composition of the catalyst and the temperature of the synthesis (Table 2). The nature and concentration of the catalyst components also have an appreciable influence on the composition of the PA.

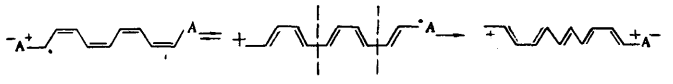
The quantitative ratios of the *cis*- and *trans*-isomers found by different workers differ significantly; this is associated with the use of different methods for the determination of the relative absorption coefficient $K_{trans/cis}$, whose values are 1.05 (Shen et al.[47]), 1.66 (Gibson et al.[176]), etc. The question concerning the mechanism of the *cis*–*trans* isomerisation is not as yet entirely clear. Probably, after the transfer of one electron to the dopant with participation of another electron and a π electron of a neighbouring carbon atom, a new double bond is formed; this process, in which the newly formed unpaired electron is involved, then develops further until the encounter with the dopant or another free electron:[177]



Table 2. The content of the *cis*-isomer (%) of polyacetylene as a function of the nature of the catalyst and the temperature of the synthesis.

Catalyst	Temperature of the synthesis, °C					Refs.
	−78	−18	0	+20	+100	
$Ti(OBu)_4$–$Al(C_2H_5)_3$	98	95	79	59	7,2	[135]
$Co(NO_3)_2$–$NaBH_4$	94	72	45	30	—	[75, 84]
WCl_6–Ph_4Sn	—	—	—	10	—	[52]
$MoCl_5$–Ph_4Sn	—	—	—	10	—	[52]
$Ti(CH_2$–$C_6H_5)_4$	—	—	—	40	—	[52]

In the presence of an acceptor, in the first stage the *cis*-transoid form is converted into the unstable *trans*-cisoid form, which constitutes an excited state of the initial form and then, as a result of rotation about two single bonds, sections with the *trans*-structures are formed:



The view has been expressed in the literature that the crystal structure of the catalyst produces a planar structure of the PA. The subsequent organisation of the polymer chains depends on the rates of polymerisation and crystallisation, changes in which can lead to sharp changes in the morphology.[38] It has been stated[38] that the concentration of the Ziegler–Natta catalyst has little influence on the PA morphology, while an increase in the ageing time leads to more appeciable changes. The influence of the catalyst on the structure and properties of PA has been investigated in greater detail.[15,16,28] Our studies have shown that the morphology of PA is influenced by the catalyst concentration and the composition of the ligand shell, but especially marked influence is shown by the nature of the metal in the catalytic cluster.[178,179]

The IR spectra of PA contain the following absorption bands: at 440 cm^{-1} (deformation vibrations of the C–C–C fragment), 740 and 1015 cm^{-1} (out-of-plane deformation vibrations of the C–H bond in the *trans*- and *cis*-forms respectively), 1118 cm^{-1} (C–C deformation vibrations), 1249 and 1329 cm^{-1} (in-plane C–H deformation vibrations), 1292 cm^{-1} (out-of-plane C–H vibrations), 3013 cm^{-1} (C–H stretching vibrations characteristic of the *trans*-structure), and 3044 and 3057 cm^{-1} (stretching vibration characteristic of the *cis*-structure).[175] The quality of the spectra increases when thin polymer films, obtained by sputtering the freshly prepared gel onto glass of the KRS type, are investigated. The doped specimens are distinguished by a characteristic absorption due to soliton modes in

the regions of 1370 and 900 cm^{-1}.[147] The photoacoustic IR spectroscopic method (PAIR) makes it possible to investigate PA powders and to detect 1150 and 1920 cm^{-1} absorption regions, which are weakly shown when other methods are used.[137] In combination with Raman spectra, the PAIR method permits a fairly profound investigation of the structures of insoluble and infusible polymers in the form of both powders and films.[17,136-139]

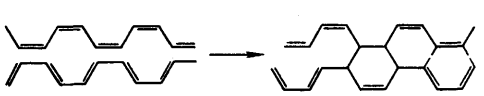
In order to determine the molecular weight and the molecular weight distribution in PA and also in order to characterise quantitatively the cross-links and other features of the structure, it is necessary to hydrogenate or chlorinate the initial polymer. These methods make it possible to convert PA into soluble derivatives. The sodium- or potassium-doped PA is hydrogenated by hydrogen at pressures up to 100 atm.[180] The PA films obtained in the presence of the $Ti(OBu)_4-AlR_3$ catalyst are treated with a solution of potassium naphthalide in THF for 1 h and are then hydrogenated for 20 h at 170–260 °C under pressure of 30 atm. The resulting product with $M_n \cong 10^4$, soluble in tetralin, is polyethylene.[180,181] A residual absorption in the region of 965 cm^{-1}, corresponding to the deformation vibrations of the C–H group and the double bond, is observed in the IR spectra. The presence of a doublet in the regions of 720 and 730 cm^{-1}, corresponding to the vibrations of the CH_2 group, makes it possible to estimate the degree of crystallinity of the specimen, which is approximately 50%. It has been suggested that a linear product is formed in the synthesis of PA in the presence of a Ziegler–Natta catalytic system,[180,182] but the considerable scatter of the yields of the soluble hydrogenation products (from 5 to 80%) suggests the appearance of cross-links in the course of the segregation of the PA.[181]

The melting point of the soluble fraction of the polyethylene obtained is 118–122 °C, the molecular weights are $\overline{M}_w$ = 6000 to 7000 and $\overline{M}_n$ = 14 100–18 700, and the ratio of the number-average and weight-average molecular weights in different specimens varies from 2.4 to 3.14.[124,130,180] Although the form of the molecular weight distribution does not change on hydrogenation of PA in the temperature range 195–260 °C,[180] nevertheless this does not rule out the possibility of cross-linking in the course of the hydrogenation process and also of the degradation of the polymer chain.

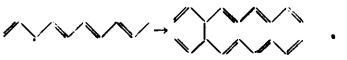
According to data obtained by the radioisotope method, the molecular weight of PA varies from 2.2×10^4 to 7.7×10^4 when the temperature of the synthesis is changed from −7° to 25 °C.[34] Polyacetylene with an end group containing tritium or labelled carbon can be obtained by adding an excess of CH_3OT or carbon-labelled CO_2 to the reaction system after the synthesis.[34,183]

Soluble derivatives of PA can be best obtained by chlorinating freshly prepared specimens in suspension in chloroform or carbon tetrachloride at low temperatures.[79] The molecular weight of the chloroform-soluble fraction of the polymer synthesised in the presence of the $Ca(NO_3)_2-NaBH_4$ catalyst is 10^4.[79] Chlorination of the freshly prepared PA suspension at low temperatures makes it possible to reduce the contribution of the possible degradation processes. However, in this case the scatter of the yields of the soluble products is observed, which is a consequence of the occurrence of secondary cross-linking processes in the ageing of the polymer. The soluble fraction of the chlorinated PA diminishes appreciably after the *cis–trans* isomerisation.[74,134]

PA can be cross-linked via the Diels–Alder reaction,[27]



or as a result of the recombination of the radical centres formed in the *cis–trans* isomerisation:



The first process is indicated by a decrease in the amount of the soluble fraction of the chlorinated polymer during the ageing of PA. The probability of the second process increases in thermal or photochemical isomerisation.[79] On oxidation or reduction of the cross-linked polymers, there is a possibility of the formation of structures of the type of Hafner salts.[27,184] The possibility of cross-linking in the course of *cis–trans* isomerisation when unpaired spins appear has been confirmed by quantitative quantum-chemical calculations for a modified diatomic overlap.[74] Attempts have been made to find a correlation between the structural defects in *trans*-PA associated with the cross-links and the vibrational spectra.[38] The attempts to characterise PA in terms of the conjugation length have shown that specimens synthesised in different laboratories have different distributions even when the same method is used. According to Raman or IR spectroscopic data, the breakdown of conjugation is not associated with oxidation in the presence of cross-links.[185] It has been suggested that this is explained by conformational defects (for example, the twisting of the chains) or the inclusion of *cis*-units in the *trans*-chain of the polyene.[185] The appearance of cross-links diminishes the length of the conjugated sections and influences greatly the mechanical and electrophysical properties of PA.[134]

Another defect influencing the properties of PA arises on partial reduction of the double bond. NMR studies using PA enriched in the ^{13}C isotope made it possible to observe a weak signal in the region of 47 p.p.m., which was attributed to methylene groups; the concentration of the latter was 3–4 mole per cent.[15] The possibility of the reduction of double bonds is also indicated by the elemental composition of PA obtained in the presence of Ziegler–Natta catalysts ($CH_{1.03}$): according to different data, the H : C ratio varies in the range from 1.01 to 1.09.[186] The signal due to the CH_2 groups is particularly strong in the ^1H NMR spectra of chlorinated PA in the range 1.2–1.6 p.p.m. Partial reduction of PA can occur even during synthesis in the presence of both Ziegler–Natta catalysts and Group VIII metals. This has also been confirmed by the results of the ozonolysis of *cis*- and *trans*-PA. The final product of the hydrolysis of the *cis*- and *trans*-isomers is the ester $CH_3COO-COOCH_3$ formed in 98.55–99.52% yield, which confirms the linearity of the structure.[73] The presence of the hydrogenated $-CH_2-CH_2-$ units and also of cross-links leads to the formation, after treatment with diazomethane, of additional esters, $CH_3OOCCH_2COOCH_3$ and $CH_3.COOCH_2COOCH_3$, in yields of 0.1–0.5 and 0.23–1.04% respectively.[73] Bearing in mind the high reproducibility of the experimental results, one can assume that an increase in the number of cross-links by a factor of 2–4 occurs during polymerisation. The appearance of defects in the PA structure, including the formation of cross-links and the occurrence of sp^3-hybridisation is indicated also by X-ray diffraction data.[39,187]

The study of electron diffraction and X-ray diffraction analysis of thin oriented PA films have revealed the presence of an orthorhombic unit cell and orientation of the chain axis along the fibrils.[185,188] In the crystalline state, the *cis*- and *trans*-isomeric forms of the chain have different symmetries and repeat distances of 4.36 Å for four CH groups and 2.46 Å two CH groups respectively. It follows from the analysis of the intensity integrals for the powder X-ray diffraction patterns in the crystalline and amorphous regions that the degree of crystallinity of the films is 70–90%. The diffuse halo (at about 4.0 Å) is close to the strong interplanar reflections at 3.81 Å for the *cis*-structures and at 3.72 to 3.56 Å for the *trans*-structures. The disorder in the amorphous region is caused by the chain ends and the sp^3-hybridisation of the carbon atoms. It follows from X-ray diffraction data that the *trans*-cell contain 7% of the structure

of the disordered *cis*-cell and that in the film there are no isolated amorphous or crystalline regions, although a PA structure with single crystals incorporated in the polymer matrix has been proposed.[27]

Doping leads to the formation of new crystal structures inserted between the planes of the initial lattice, whose contribution depends on the diameter of the fibrils, the number of cross-links, the size of the dopant, etc. The inhomogeneity caused by the slow diffusion of the dopant in the fibril also influences the final crystal structure of PA. The distances between the inclusions of the dopant, which is believed to aggregate into packs along the same axis, is between 20 and 60 Å.[187] The interplanar spacings, which are 7.95 Å for I_3^-, 8.3 Å for ClO_4^-, and 9.3 Å for $FeCl_4^-$, can be interpreted as the distances between two dopant-enriched planes separated by PA chains.[187] The X-ray diffraction parameters for different types of PA obtained by the method described above (Table 3) differ somewhat; this is associated with the nature of the catalytic system used and with the method of preparation of the specimens for the investigations. The apparent size of the crystallites, determined from the width of the reflections for PA obtained in the presence of Ziegler catalysts, is 60 Å;[189] for the PA obtained in the presence of Group VIII metals, it reaches 100 Å and more.[178,179]

Table 3. The unit cell parameters of polyacetylene.

Catalyst	Unit cell parameters, Å			Crystal system	Refs.
	a	*b*	*c*		
cis-PA					
$Ti(OBu)_4$—$Al(C_2H_5)_3$	7.68	4.46	4.48	orthorhombic	[6, 190]
»	7.61	4.47	4.39	»	[191]
»*	7.74	4.32	4.47	»	[67, 85]
$Co(NO_3)_2$—$NaBH_4$*	7.76	4.32	4.47	»	[27]
$TiO(Bu)_4$—$Al(C_2H_5)_3$**	5.12	—	4.84	hexagonal	[129]
trans-PA					
$Ti(OBu)_4$—$Al(C_2H_5)_3$	7.32	4.24	2.46	rhombic	[188]
»***	4.24	7.32	2.46	monoclinic	[39]
$Co(NO_3)_2$—$NaBH_4$	5.62 (6.62)	4.92	2.59	orthorhombic	[79, 142]
Poly-BTFM	7.32	4.24	2.46	monoclinic	[56]
Catalyst based on lanthanide metals	5.08	5.44	9.52	rhombic	[192]

*According to electron diffraction data.
**Block-copolymers of the single crystal.
***Oriented films.

The morphology of PA has been mainly investigated using scanning electron microscopes, but more extensive information has been obtained on high-resolution transmission microscopes.[193] The formation of lamellar particles of irregular shape and with a thickness of 50–100 Å, which, by joining together, form loose fibril-like structures where the chain axes are perpendicular to the fibril axes, has been noted by Wegner and co-workers.[27,79,85,194] However, it was subsequently shown fairly convincingly by electron diffraction and scanning microscope methods that the chain axes in the films are parallel to the axes of the fibrils.[190,191] It is essential to note that the study of the morphology of PA by transmission or scanning electron microscopy makes it necessary to master a fine technique of the preparation of the specimens; the frequently observed "kebab" structures[188] or lamellar formations, thickened regions comprising knots of individual fibres and appearing on doping, as well as the "string of pearls" effect are usually associated with the metal deposition technique (Au : Pd).[195] The conditions leading to photographs in which the initial morphology is masked have been discussed. The size of the fibrils can be diminished by carrying out the polymerisation in the presence of various copolymers, which prevent their formation. The morphology of PA changes in the doping process and a new highly crystalline structure appears. The pattern in the distribution of iodine, used as the dopant, indicates the absence of the segregation of particles.[196]

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The dependence of the PA structure on the composition and concentration of the catalyst, the reaction temperature, and the nature of the monomer gives rise to the hope that the possibilities for the synthesis of polymers of this class are still far from being exhausted. Further development of the synthesis of polymers of the acetylene series will depend on the practical requirements which they will have to meet in the creation of specific instruments or devices

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Modern Methods of Synthesis of Modified Glycerophospholipids

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The advances in the synthesis of modified glycerophospholipids of different structure are surveyed. An attempt has been made at a general classification of these compounds. Questions concerning the problem of whether or not various methods of synthesis can be used on a preparative scale are examined.
The bibliography includes 233 references.

CONTENTS

I. Introduction 382
II. Classification and strategy in the synthesis of modified glycerophospholipids 382
III. Modified aliphatic acids 383
IV. General procedures in the synthesis of modified glycerophospholipids 385

I. INTRODUCTION

The vigorous development of bio-organic chemistry during the last decade has led to the creation of preparative methods of synthesis of virtually all principal classes of substances found in living organisms, including glycerophospholipids (PL).[1] However, the tasks faced by investigators have increasingly required the use of modified PL. The applications of modified PL are extensive. They serve as instruments for research into (a) the metabolism of individual representatives of PL,[2] (b) the molecular organisation of submolecular structures whose composition includes PL (membranes, blood plasma lipoproteins, etc.) and the processes incurring in them,[3-15] and (c) enzymes associated with the metabolism of PL;[16-25] furthermore, certain representatives of modified PL are of interest as potential therapeutic agents,[26-31] while a number of PL analogues, which can be immobilised on solid carriers, are of interest as ligands in affinity chromatography for the isolation of various proteins exhibiting an affinity for PL.[32-39]

In principle, traditional methods of synthesis of PL can be used to obtain modified PL,[1] but in most cases special procedures are required, taking into account the specific features of both the label and of the methods used in their subsequent application. The fact that the majority of the labels are relatively difficult to obtain is also reflected in the strategy of the synthesis. It is believed to be preferable to introduce the label in the last stages of the synthesis, which reduces the possibility of the modification of the label (which is as a rule labile) during synthesis and permits an economical utilisation of the labelled intermediates.

II. CLASSIFICATION AND STRATEGY IN THE SYNTHESIS OF MODIFIED GLYCEROPHOSPHOLIPIDS

As the term PL embraces a large group of compounds with extremely varied structures, it is essential to deal with the classification of such PL before considering the methods of their synthesis. PL can be classified in terms of various features: in terms of the aims of the modification (and hence the way in which they are subsequently used), in terms of the site of the modification, and in terms of the type of modification (the type of label).

In terms of the aims of the modification, it is possible to distinguish two types of modified PL: labelled PL (as a rule PL having the natural structure and containing the label or reporter group; they are normally employed as lipid-specific probes or labels closely imitating the corresponding lipids in terms of their properties) and structural analogues of PL (PL in which the structure of the hydrophobic or polar component of the molecule and/or the type of the chemical bond between them has been modified in order to impart to them properties different from those of the natural PL).

Labelled PL can be subdivided further in terms of the type of label into radioisotope-labelled, spin-labelled (those whose composition includes stable nitroxy-radicals), fluorescence-labelled, and photoreactively labelled PL (containing photoreactive groups), PL with NMR-labels (detected with the aid of NMR), and PL with electronically dense labels.

In terms of the site of the modification, all the modified PL can be divided into two classes: (1) derivatives of lipids having the natural structure (this class includes the majority of the labelled PL) and (2) PL with an altered "skeleton". The former are subdivided in their turn into PL modified in the hydrophobic or polar components (Fig.1) and the latter into derivatives of 2-glycerophosphate,[25, 40-42] PL modified in the glycerol residue,[16,20,21,43-54] and PL modified in the phosphoester group.[55-71]

In the general case, the synthesis of modified PL reduces to the synthesis of the initial compounds and their interaction (key stage). The starting materials for the synthesis of the modified PL can be subdivided into two types: structures carrying the label (or the modified fragment), i.e. modifying compounds, and "skeletal" structures which determine the type of the required PL and the site of the label in its molecule.

As regards strategy, the methods of synthesis of modified PL can be arbitrarily divided into synthetic (the assembly of the PL molecule from elementary components: glycerol, aliphatic acids, etc.), semisynthetic (modification of natural PL with the aid of chemical and enzymic reactions), and biological. The semisynthetic methods are the most effective and for this reason they have been used recently with increasing frequency for the modification of PL. However, in a number of instances, for example, in the synthesis of PL modified in the glycerol residue[16,20,21,43-54] and in the phosphoester group[16, 22-24,44,55-72] or isomeric PL,[16,25,40-42,44] total chemical synthesis is essential. The biological methods are more rarely used preparatively[73] and we shall therefore confine ourselves to the consideration of the first two most often used methods for the modification of PL.

To facilitate the use of the present review and to reduce its size, we propose the following procedure for indexing the references. A four-digit number indicating the structure and method of synthesis of the modified PL (see Table 1 and the list of literature references) is assigned to each reference to the synthesis of modified PL (in the list of literature references, it is written at the end of the reference in angular brackets). The first digit indicates the class of the PL, the

second the type of modification (vertical columns in Table 1 with numbers ranging from 0 to 9), and the third the site of the modification (in conformity with Fig.1). We introduce the fourth digit in order to reflect as far as possible the position of the key stage (usually the reaction involving the introduction of the modifying fragment) in the synthesis of the modified PL (Fig.2).

For example, the designation <2044> corresponds to the synthesis of phosphatidylethanolamine (PE) fluorescence-labelled in the polar component, the key stage in the synthesis of which involves a reaction in the polar head (evidently *N*-alkylation or *N*-acylation). Thus it is possible to find readily from Table 1 the reference to a given feature and the list of literature references contains coded information about the contents of a particular communication.

III. MODIFIED ALIPHATIC ACIDS

One of the main types of initial compounds carrying a modified fragment (or label) are modified (labelled) aliphatic acids (ALA). In the synthesis of modified PL, fluorescence-labelled, spin-labelled, and photoreactively labelled ALA (Table 2), as well as isotope-labelled ALA are most widely used.

One of the general and widely employed methods for the introduction of isotope labels (^2H, ^3H) into the hydrocarbon chain of the ALA involves the hydrogenation of unsaturated acids in a $^2H_2$ or $^3H_2$ atmosphere. It is then possible to obtain both saturated ALA [145-147] and fully *cis*-monoene or *cis*-polyene ALA from the corresponding acetylenic acids by hydrogenating the latter in the presence of the Lindlar catalyst.[134-145]

The ^1H atoms can be substituted by the radioactive isotope ^3H also by heterogeneous catalytic isotope exchange with gaseous tritium[148,149] or by the method involving thermal activation of tritium.[132] Randomly tritium-labelled ALA are then obtained. In the case of deuterium, the employment of the heterogeneous catalytic isotope exchange method makes it possible to obtain perdeuteriated ALA with an isotopic purity in excess of 99%.[150,151]

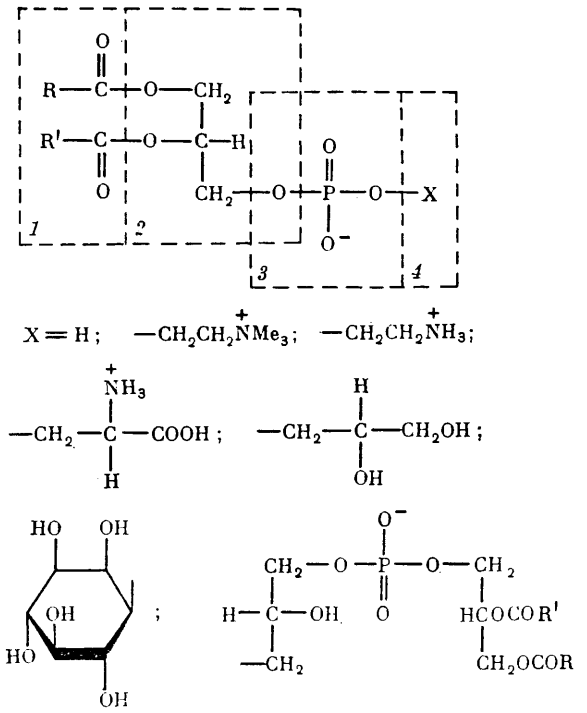


Figure 1. The possible sites of the modification of PL: 1) hydrophobic component (acyl residues); 2) glycerol residue; 3) phosphodiester/phosphomonoester group; 4) polar component.

Apart from the methods listed above, there exist also various procedures which make it possible to introduce the ^{13}C, ^{14}C, ^2H, or ^3H labels at the end,[143,145,152,153] beginning,[154] or middle of the

Table 1. Notation for the references to the synthesis of the modified PL and ALA.

PL	No.	Labels						Structural analogues			
		fluorescent	spin	photoreactive	radioisotope	NMR	electron-dense	3-glycerophosphate derivatives	2-glycerophosphate derivatives	modified in glycerol residue	modified in phosphoester group
		0	1	2	3	4	5	6	7	8	9
PC	1	3, 5, 7—11, 19, 74—76, 78—81, 85, 87, 88, 90, 92—99, 101—104, 106—111, 182, 213	17, 113, 114, 117, 121, 122, 125, 127, 129, 186—188	4, 11—14, 131—142, 144, 182, 202	4, 11, 18, 23, 104, 132, 134, 136, 138, 139, 146, 147, 182, 189, 191, 202, 225, 227, 228	144, 151, 158—160, 190, 209, 224, 226, 227	161	2, 32—38, 55, 162—169, 183, 185, 192, 217, 218	16, 25, 40—42, 44	16, 20, 21, 43—48, 51, 53	15, 16, 24, 44, 55, 61, 63, 66, 67, 70, 71, 231,232
PE	2	6, 78 87, 88, 99, 104, 109, 170—172, 174, 177, 180, 181, 193, 200, 201	115, 116, 118, 119, 129, 175, 188, 199, 207	12, 131, 135, 137, 178	22, 72, 146, 189, 211, 212	—	204	26, 27, 39, 164, 165, 176, 179, 214,215, 216—219, 222	40	20, 21, 53, 54	60, 62, 63, 67, 71
PS	3	18, 99, 173	129, 175, 187, 188	—	18, 189, 197, 212	210	—	176	—	52	—
PG	4	7, 99	188	194	—	—	—	—	—	—	—
PI	5	77, 88, 99, 195, 196	17, 120, 175, 196	—	73	—	—	—	—	—	—
DPG	6	88	123, 184, 198	203	—	—	—	—	—	—	—
PA	7	7, 99, 105, 109, 170	186—188, 205—207	—	189	—	—	28—31, 58,59, 164, 165, 220, 221, 223	—	49, 50, 65, 68	56—59, 64, 65, 67—69, 231
ALA	8	3, 5, 74, 82—84, 86, 89—96, 100—102, 110, 111	17, 112, 113, 124—128, 130, 207	131—134, 136—140, 142—144	132, 134, 136, 138, 139, 142, 143, 145, 148—150, 152, 156, 157	144, 151, 152—155, 158	161	—	—	—	—

hydrocarbon chain of the ALA [144,153,155] and also to obtain ALA labelled at the carbonyl carbon atom.[142,145,156,157]

Apart from isotope labels, certain heteroatoms, for example ^{19}F, whose chemical shift is sensitive to differences between the outer and inner surfaces of vesicles, can be introduced as NMR-labels.[158-160]

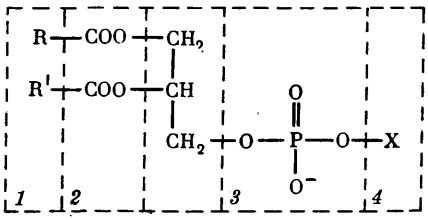


Figure 2. The types of key reactions in the synthesis of modified PL as a function of their location: 1) reactions in the hydrocarbon chains of the acyl residues of the PL; 2) formation of ester (thioester, amide, or others) bonds; 3) phosphorylation and reactions of phosphorus(III) derivatives; 4) reactions in the polar head of the PL.

Table 2. Labelled carboxylic acids most promising for the synthesis of modified PL.

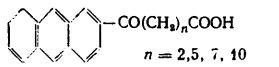
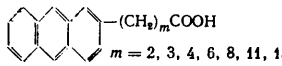
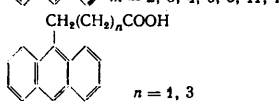
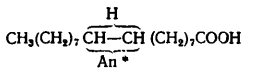
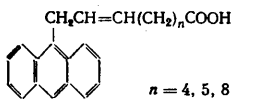
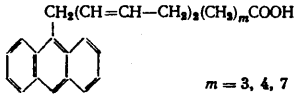
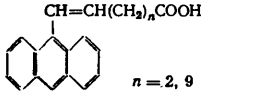
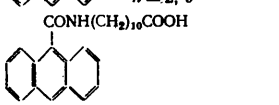
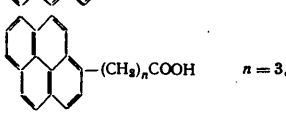
Name	Formula	Refs.
	Fluorescence-labelled	
α-Parinaric		[74–79]
β-Parinaric		[74–76, 78, 80]
ω-(2-Anthroyl)-carboxylic	 $n = 2,5, 7, 10$	[81–84]
ω-(2-Anthryl)-carboxylic	 $m = 2, 3, 4, 6, 8, 11, 13, 16$	[7, 82, 89–91]
ω-(9-Anthryl)-carboxylic	 $n = 1, 3$	[89]
9(10)-Anthryl-stearic		[85–88]
ω-(9-Anthryl)-*cis*-monoenoic	 $n = 4, 5, 8$	[92]
ω-(9-Anthryl)-*cis*-dienoic	 $m = 3, 4, 7$	[92]
ω-9-(Anthrylvinyl)-carboxylic	 $n = 2, 9$	[93, 94]
N-(9-Anthroyl)-11-amino-undecanoic		[93]
ω-(1-Pyrenyl)-carboxylic	 $n = 3, 5, 9$	[5, 95–100]

Table 2 (contd.).

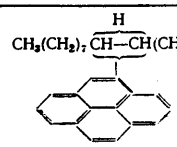
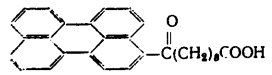
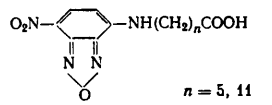
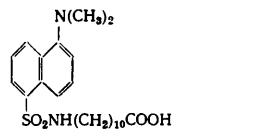
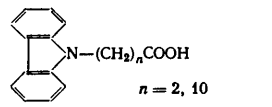
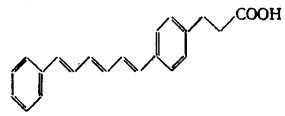
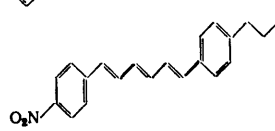
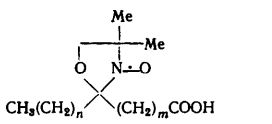
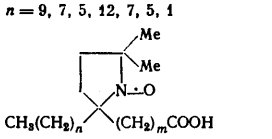
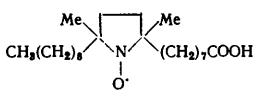
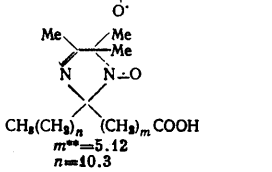
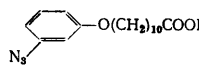
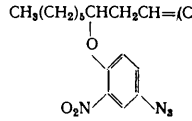
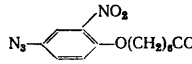
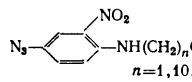
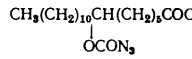
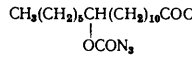
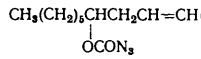
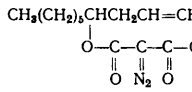
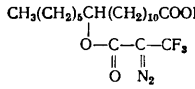
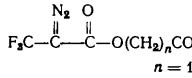
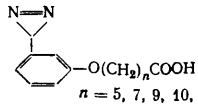
Name	Formula	Refs.
9(10)-(4-Pyrenyl)-stearic		[88]
9-(3-Perylenoyl)-nonanoic		[101]
N-NBD-amino-carboxylic	 $n = 5, 11$	[102–106]
N-Dns-11-amino-decanoic		[107]
N-(9-Carbazolyl)-carboxylic	 $n = 2, 10$	[108, 109]
β-[4-(Phenylhexatrienyl)phenyl]-propionic		[110]
β-[4-(4-Nitrophenylhexatrienyl)-phenyl]-propionic		[111]
	Spin-labelled	
Doxylcarboxylic	 $m^{**} = 4, 6, 8, 3, 8, 10, 14$ $n = 9, 7, 5, 12, 7, 5, 1$	[112–123]
Proxyl-carboxylic	 $m^{**} = 5, 7, 14, 15$ $n = 10, 0, 0, 0$	[124, 125]
cis(*trans*)-10-Azetoxyeicosanoic		[126, 127]
Iminoxycarboxylic	 $m^{**}=5.12$ $n=10.3$	[128–130]
	Photoreactively-labelled	
16-Azido-palmitic	$N_3(CH_2)_{15}COOH$	[4]
12-Azido-stearic	$CH_3(CH_2)_5CH(CH_2)_{10}COOH$ N_3	[131, 132]
12-Azido-oleic	$CN_3(CH_2)_5CHCH_2CH=CH(CH_2)_7COOH$ N_3	[4, 131, 133]
18-Azidolinoleic	$N_3(CH_2)_5(CH=CHCH_2)_2(CH_2)_6COOH$	[4, 134]

Table 2. Labelled carboxylic acids most promising for the synthesis of modified PL.

Name	Formula	Refs.
11-(*m*-Azidophenoxy)undecanoic		[135]
12-(4-Azido-2-nitrophenoxy)-oleic		[131]
7-(4-Azido-2-nitrophenoxy)-heptanoic		[135, 136]
N-(4-Azido-2-nitrophenyl)-ω-aminocarboxylic		[132, 137—139]
7-Azidocarbonyloxystearic		[170]
12-Azidocarbonyloxystearic		[140]
12-Azidocarbonyloxyoleic		[133]
12-(Ethyl-2-diazomaloyloxy)-oleic		[131, 133]
12-(2-Diazo-3,3,3-trifluoropropionyloxy)-stearic		[140]
ω-(2-Diazo-3,3,3-trifluoropropionyloxy)-carboxylic		[135, 141, 142]
ω-(*m*-3*H*-diazirinophenoxy)-carboxylic		[12, 13, 135, 142—144]

*The significance of the symbol An is indicated in Scheme 1.
**m and n are inter-related.

In order to obtain probes for the investigation of the outer structure of biological membranes by electron microscopy, an organotin analogue of ALA, namely 12,12-dimethyl-12-stannahexadecanoic acid, has been synthesised[161] and introduced into the composition of phosphatidylcholine (PC).

Since 1980, a series of syntheses of photopolymerisable ALA, containing the methacryloyloxy-group[162] or conjugated diacetylene or diene groups,[163-165] have been synthesised. Membranes made up of photopolymerised PL exhibit the properties of both the usual phospholipid double layers and certain properties (for example, resistance to the action of detergents) more characteristic of polymer membranes;[166,167] in 1985, the synthesis of PC incorporating ALA containing the thiol group at the end or beginning of the hydrocarbonchain was reported.[168,169] The liposomes consisting of such PL are capable of reversible polymerisation and depolymerisation via the thiol—disulphide oxidation-reduction cycle.

IV. GENERAL PROCEDURES IN THE SYNTHESIS OF MODIFIED GLYCEROPHOSPHOLIPIDS

The synthesis of modified PL can be conveniently considered in most cases in accordance with the site of the modification of the PL, which makes it possible to differentiate the general methods of synthesis regardless of the type of modification.

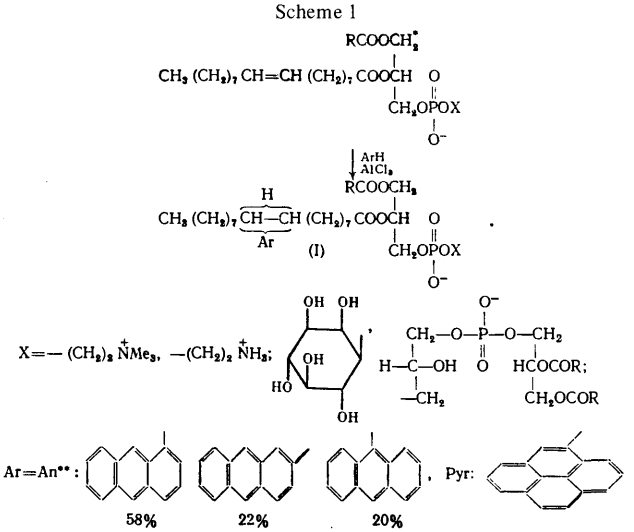
1. Synthesis of Glycerophospholipids Modified in the Hydrophobic Component

The most general feature influencing the properties of modified PL is the location of the label (modified fragment)—the hydrophobic or polar part of the molecule. Since the polar part of the molecule as a rule determines the majority of the physicochemical properties of the PL, its modification can alter significantly the behaviour of the PL molecule. For example, acylation of PE or phosphatidylserine (PS) at the amino-group[131,170-181] alters the charge and size of the polar head of the lipid molecule. Therefore, in the synthesis of labelled PL which should possess properties close to those of the corresponding natural PL, it is more desirable to modify the aliphatic acid part of the PL molecule; this is particularly justified in view of the fact that this region is relatively large and introduction of the label in this way therefore has less effect on the behaviour of the PL molecule.

(a) Addition to the C=C Bonds of the Acyl Residues in Glycerophospholipids

The introduction of the label at the double bonds of the acyl residues of the PL is the simplest method of obtaining PL modified in the hydrophobic component. The interaction of natural PL with polynuclear aromatic hydrocarbons (anthracene or pyrene) under the conditions of the Friedel—Crafts reaction yields in a single stage PL fluorescence-labelled in the hydrophobic component[85,87,88] (Scheme 1). The label in the PL (I) is then located mainly in the 2-position in the glycerol residue of the molecule (in conformity with the distribution of unsaturated ALA in natural PL).[87,88]

Scheme 1



*Oleic acid is indicated in the 2-position of the glycerol residue, since it represents more than 50% of the unsaturated acids contained in the majority of natural PL.[182]
**The ratio of the anthracene isomers was determined by ^{1}H NMR.[86]

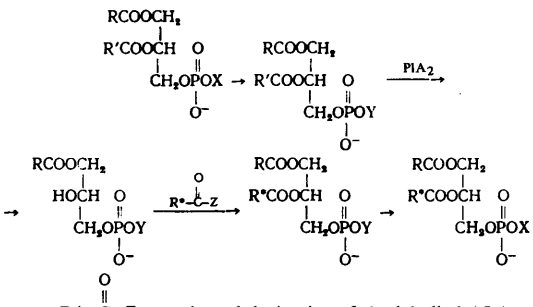
An undoubted advantage of this method is its universality: aromatic fluorophores can be introduced into the majority of natural PL.

Addition to the double bonds of the acyl residues of PL is also used to introduce isotope labels (^2H, ^3H) and certain heteroatomic labels (Br) into PL.[147,183]

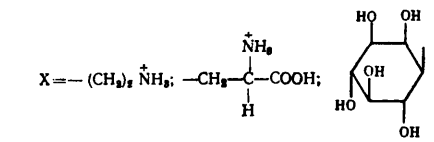
(b) Acylation of Glycerophosphates and Lysophospholipids

The commonest version of the semisynthetic method involves the introduction of a labelled ALA into lyso-PL, which is obtained by the enzymic hydrolysis of the PL using phospholipase A_2(Pl A_2) [74-79,81,90,92-95,99,101,102] (Scheme 2):

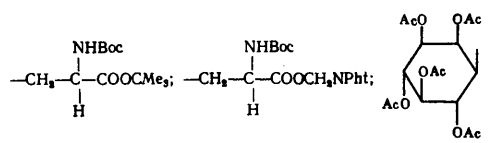
Scheme 2



R*-C-Z = activated derivative of the labelled ALA



Y = — $(CH_2)_2$NHNPS; —$(CH_2)_2$NHBoc; —$(CH_2)_2$NPht;

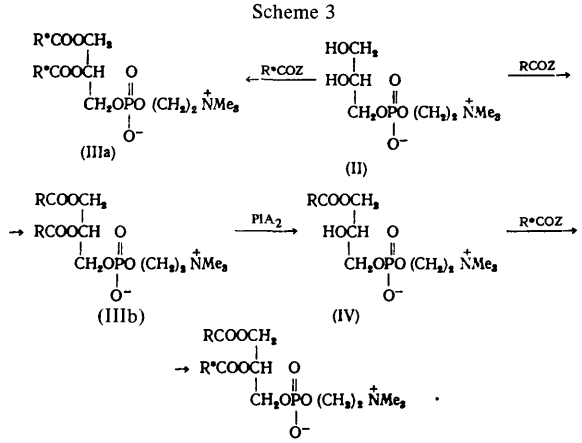


NPS = *o*-nitrobenzenesulphenyl; Boc = t-butoxycarbonyl; Pht = phthaloyl

For all the PL, except PC, it is then as a rule necessary to carry out a preliminary blocking of the functional groups in the polar component of the PL and their deblocking after the acylation of the lyso-PL (Scheme 2). The amino-groups of PE and PS are blocked by *o*-nitrobenzenesulphenyl, t-butoxycarbonyl, and phthaloyl protecting groups,[1,115,116,118,119] the carboxy-group of the PS is blocked by t-butyl and phthalimidomethyl groups,[1] the hydroxy-groups of myoinositol are protected by acetylation,[1,77,99,120] while the hydroxy-group of the glycerol residue of diphosphatidylglycerol (DPG) is not as a rule blocked[123,184] because of its insignificant reactivity.

The labelled PL obtained by this method consist of a mixture of molecular types differing in the acids in the 1-position in the glycerol residue. A procedure consisting in the alkaline hydrolysis of PC and the subsequent acylation of the ALA-labelled glycerophosphocholine (II) is used for the synthesis of the individual substances[79,80,96,135,140,158,162] (Scheme 3):

Scheme 3

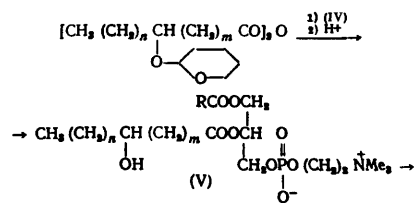


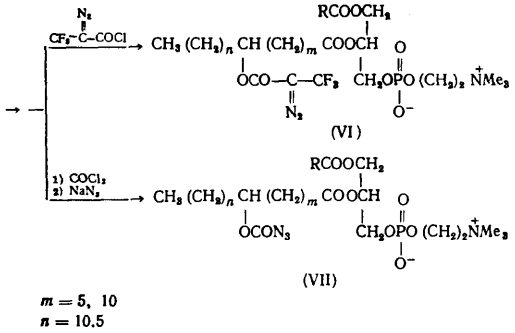
In order to obtain heteroacid PL, glycerophosphocholine (II) is acylated initially with the natural ALA, after which compound (IIIb) is hydrolysed by Pl A_2 and the lyso-PC (IV) is acylated with the labelled ALA [18,99,135,142,144,162] (Scheme 3), the reverse acylation sequence leading to PC with the label in the first acyl residue.[79,80,140,158,162]

Lyso-PL (IV) and the glycerophosphates (II) are acylated by traditional methods in the chemistry of PL.[1] The acylating agents employed are the chlorides of the modified acids[77,92,93,95,96,99,133] and also the more effective (especially in the case of ALA which are difficult to obtain and labile labelled ALA) anhydrides of the ALA in the presence of readily dissociating alkali metal salts of the ALA,[74,102,115,119,158,185] alkali metal oxides,[113,114,123,161,186,188] 4-*NN*-dimethylaminopyridine (DMAP),[79,90,99,110,111,132,135,137,140,142,144,162,189,190] or 4-pyrrolidinopyridine;[106] also used are ALA in the presence of dicyclohexylcarbodiimide (DCC) and DMAP [94,101,138,139,168] or trifluoroacetic anhydride and pyridine,[191] as well as ALA imidazolides.[80,81,93,104,105,116-118,120-122,125,127,129,136]

In many cases (especially when labile labels are used), it is useful to obtain initially the PL containing in one of the acyl residues (and sometimes in both) an active functional group (usually the hydroxy- or amino-group)[103,104,106,107,140,189] with the subsequent introduction of the label into the resulting PL molecule. Thus the photoreactively labelled PC (VI) and (VII) have been obtained by acylating the hydroxylated PC (V) with 2-diazo-3,3,3-trifluoropropionyl chloride or chloroformylated phosgene with subsequent replacement of the chlorine atom by the azido-group[140] (Scheme 4):

Scheme 4





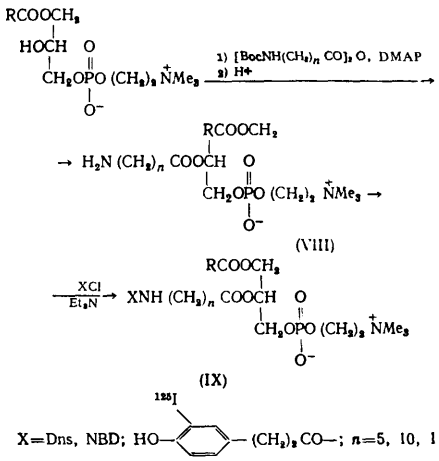
(VI)

(VII)

$m = 5, 10$
$n = 10.5$

Fluorescence-labelled PC [103,104,106,107] as well a a PC analogue containing the ^{125}I isotope (IX) [189] have been obtained by acylating (or alkylating) the amino-groups in the ω-aminoacyl residues of PC (VIII) (Scheme 5):

Scheme 5



(VIII)

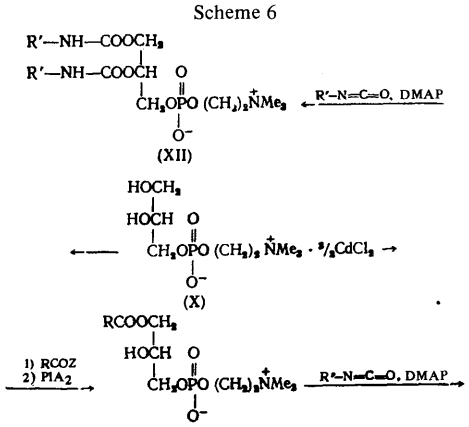
(IX)

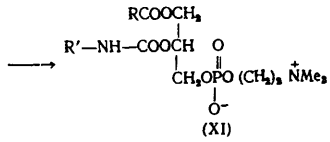
X=Dns, NBD; HO—C$_6$H$_4$—(CH$_2$)$_2$CO—; n=5, 10, 11;

Dns = 5-dimethylaminonaphthalene-1-sulphonyl (dansyl);
NBD = 7-nitrobenzo-2-oxa-1,3-diazol-4-yl

The interaction of lyso-PC (IV) or the cadmium complex of glycerophosphocholine (X) with alkyl isocyanates results in the formation of PC analogues non-hydrolysable by phospholipase A_2, in which the ester group at the C(2) atom of the glycerol residue [as in compound (XI)] or both ester groups, at C(1) and C(2) [as in compound (XII)], have been substituted by the carbamoyloxy-group[192] (Scheme 6):

Scheme 6



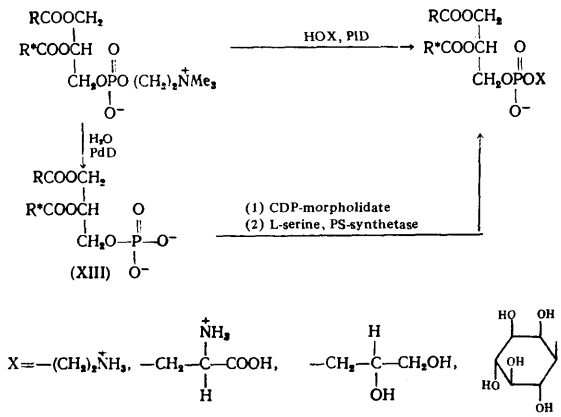


(XI)

(c) Transphosphatidylation of PC by phospholipase D

In connection with the discovery of the reaction involving the transfer of the phosphatidyl residue from one alcohol component to another, catalysed by phospholipase D, the possibilities in the synthesis of modified PL have expanded greatly. Thus conditions have been found in which phospholipase D effects the exchange of the choline group in PC for ethanolamine,[20,63,78,99,129,137,188,189,193] glycerol,[7,99,188,194] serine,[99,189] and myoinositol.[195,196] This makes it possible to unify the scheme for the preparation of modified PL: the synthesis of the labelled PC and its transphosphatidylation by phospholipase D in the presence of ethanolamine, serine, glycerol, and myoinositol or hydrolysis with formation of phosphatidic acid (PA) (Scheme 7):

Scheme 7



CDP = cytidine diphosphate

Fluorescene-labelled PE, PS, phosphatidylglycerol (PG), phosphatidylinositol (PI), and PA,[7,99,193,195,196] spin-labelled PE, PS, PG, PI, and PA,[129,186,188] photoreactively labelled PE and PG,[137,194] and also radioactive analogues of PE, PS, and PA labelled with ^{125}I [189] have been obtained by this method.

Another version of enzymic synthesis has been used to obtain PS spin-labelled in the hydrophobic component[187] or radioisotope-labelled in the polar component:[197] the conversion of PA (XIII) into CDP-diglyceride followed by its interaction with L-serine in the presence of PS-synthetase (Scheme 7).

2. The Synthesis of Glycerophospholipids Modified in the Polar Head Groups

The presence in the polar components of many PL of active functional groups (hydroxy- or amino-groups) has led to a convenient and relatively simple way of modifying them.[131,170-181,198-204] However, at the same time taditional synthetic methods have continued to be used for the preparation of PL modified in the polar component.[1,28,31,58,59,94,205-223]

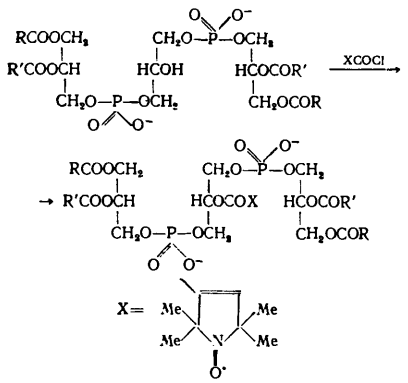
The modification of PL in the polar head groups is used to obtain not only membrane probes[131,170-178,180,198-213] but in recent years has been employed with increasing frequency for the synthesis of various lipophilic physiologically active substances, for example, antioxidants

(phosphatidylhydroquinones),[58,59] the antiviral preparation acyclovir,[31] immunologically active PL analogues containing various haptens in the polar component,[179,181,220,221] nucleotido-PL with antitumour activity,[28-30] etc.

(a) Acylation of the Hydroxy-groups in the Polar Head of the PL

Only a few examples of the direct introduction of the label into the polar component of DPG and PI are known. In the former case,[198] the natural DPG was acylated with the chloride of 2,2,5,5-tetramethyl-*N*-oxypyrroline-3-carboxylic acid in the presence of pyridine (Scheme 8):

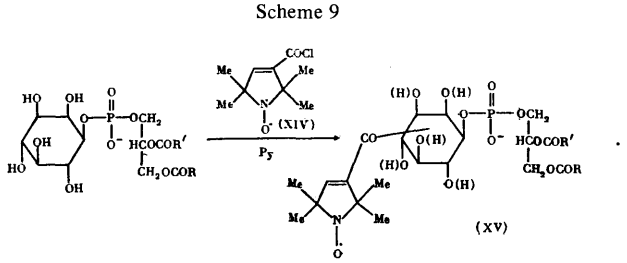
Scheme 8



However, it is known that the hydroxy-group of DPG is difficult to acylate under these conditions[123] and the attainment of high yields in the acylation reaction is therefore unlikely in the given instance. The synthesis of photoreactive analogues of DPG containing the 4-azido-2-nitrophenyl group in the polar component of the molecule has also been reported.[203]

The acylation of PI with an equimolar amount of the acid chloride (XIV) yielded compound (XV) with an indefinite position of the label in the cyclitol ring[175] (Scheme 9):

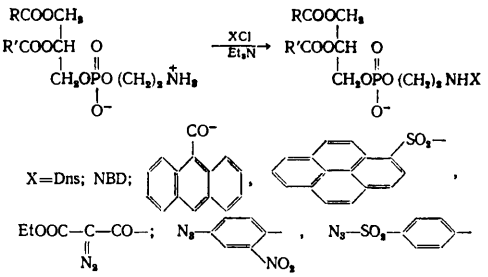
Scheme 9



(b) N-Acylation and N-Alkylation of PE and PS

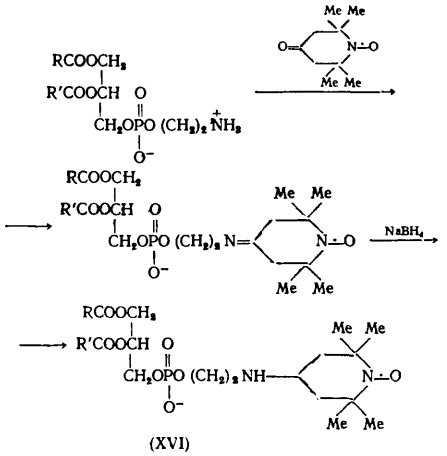
The reactions involving the acylation and alkylation of the amino-groups are used very often for the direct introduction of the label into the polar component of PE or PS. *N*-Dns-PE,[170-173] *N*-NBD-PE,[200] *N*-(9-anthroyl)-PE,[174] *N*-(1-pyrenesulphonyl)-PE,[177] *N*-(ethyl-2-diazomalonyl)-PE,[131,178] *N*-(azido-2-nitrophenyl)-PE,[131] and *N*-(4-sulphonylazidophenyl)-PE [202] (Scheme 10), as well as *N*-Dns-PS,[173] *N*-NBD-PS,[18] and *N*-biotinyl-PE and *N*-biotinyl-PS [176] have been obtained by this method:

Scheme 10



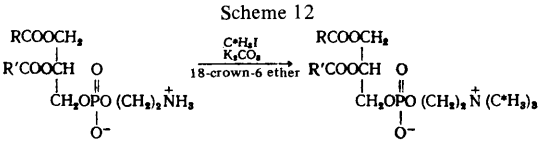
The method involving the reductive alkylation of the amino-group in PE has also been used to obtain the paramagnetic analogue (XVI) of PE [199] (Scheme 11):

Scheme 11



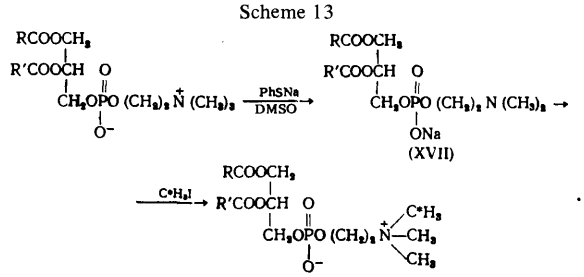
One of the methods of synthesis of PC, isotopically-labelled in the choline group, consists in the *N*-methylation of PE with labelled methyl iodide in the presence of crown-ether and anhydrous potassium carbonate[224] (Scheme 12):

Scheme 12



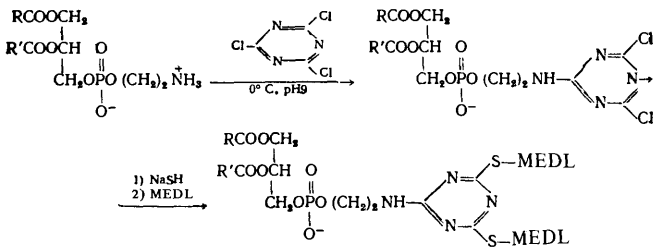
Partial demethylation of PC in the presence of sodium thiophenoxide in dimethyl sulphoxide (DMSO) followed by the methylation of the dimethylamino-derivatives (XVII) with labelled methyl iodide likewise leads to isotope-labelled PC [225-228] (Scheme 13):

Scheme 13



One of the few examples of the synthesis of PL with an electronically dense label is based on the arylation of PE with cyanuric chloride and subsequent replacement of the Cl atoms by SH groups and the reaction with MEDL† [204] (Scheme 14):

Scheme 14



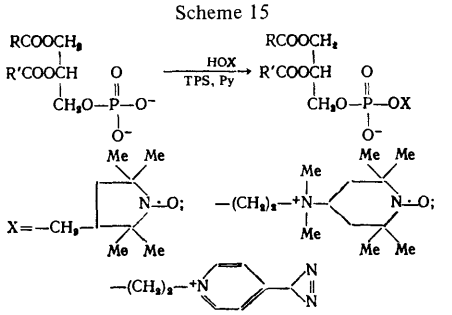
(c) Phosphorylation

PL modified in the polar component are frequently obtained using classical methods for the phosphorylation of glycerol derivatives (1,2-diglycerides, 1,2-*O*-isopropylidene-*sn*-glycerol, or halogenohydrins of 1,2-diglycerides): the phosphorochlorinate method, the silver salt method, and the interaction of phosphomonoester derivatives (usually PA) with the alcohol components in the presence of various activating agents.[28,31,205-223]

Thus, PC, PE, *N*-methyl-PE, and *NN*-dimethyl-PE analogues with different distances between the P and N atoms have been obtained by the phosphorochloridate method;[217-219] the silver salt method has been used to obtain a fluorescent analogue of PC containing the 2-[3,6-bis(dimethylamino)-10-acridino]ethyl group,[213] two immunoactive analogues of PL containing 3β-cholesterol and 3β-hydroxynorpregnen-5-ene,[220,221] several isotope-labelled PL,[211] and a series of PE analogues with different distances between P and N atoms.[214,215]

In the method using activating agents, the phosphomonoester component is usually activated with 2,4,6-triisopropylbenzenesulphonyl chloride (TPS).[109,142,205-210] The free-radical analogues of PA [205,207] and PC,[208] the photoreactive analogue of PC [142] (Scheme 15), and a series of isotope-labelled PC [209] and PS [210] have been obtained by this method:

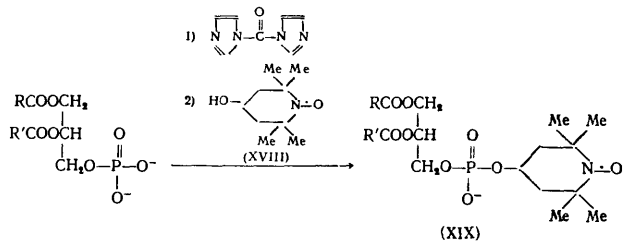
Scheme 15



†MEDL is the electron-dense mercarbide label (organomercury compound having not less than four C—Hg—X groups, where X is an acid anion).[204]

In the interaction of PA with secondary alcohols, this method proved to be relatively unsuitable owing to the low reactivity of these compounds under phosphorylation conditions, which in fact accounts for the difficulty of obtaining the nitroxy-derivative of PA of type (XIX).[205] In order to increase the efficiency of the phosphorylation of secondary alcohols, in particular of the alcohol (XVIII) with an iminoxy-group, use was made of the highly reactive PA imidazolides obtained without isolation by treating the reaction mixtures with carbonyl bisimidazole[206] (Scheme 16):

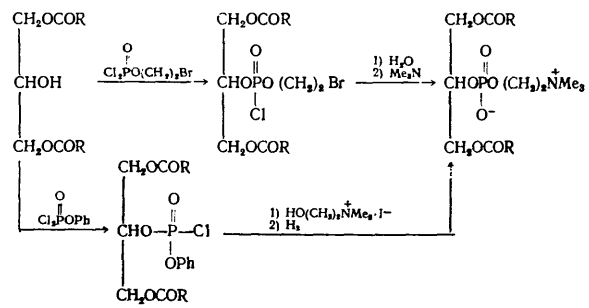
Scheme 16



3. Synthesis of Isomeric PL—Derivatives of 2-Glycerophosphate

A general method of synthesis of structural isomers of PL involves the phosphorylation of 1,3-diacylglycerols[40] by the phosphorylating agents used in the synthesis of PL having the natural structure[41,42] (Scheme 17)

Scheme 17



Isomeric PC and PE have been obtained in this way,[40-42] but the yields are as a rule lower in this instance than in the phosphorylation of the primary hydroxy-group.[40]

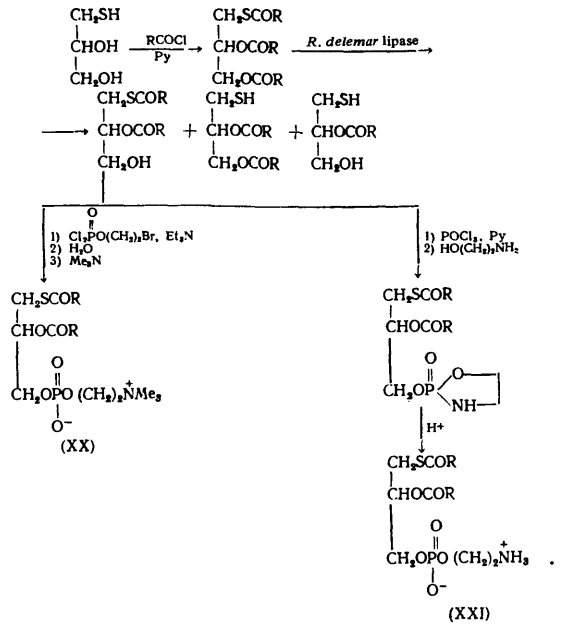
Isomeric PL are analogues of substrates of phospholipases which are hydrolysed much more slowly than the natural PL.[16]

4. Synthesis of PL Modified in the Glycerol Residue

PL analogues in which the ester linkage in one of the positions in the glycerol residue of the molecule has been replaced by the thioester linkage[21] or a phosphoester linkage has been replaced by a thiophosphoester linkage[20-43] are convenient substrates for spectrophotometric studies on phospholipases.

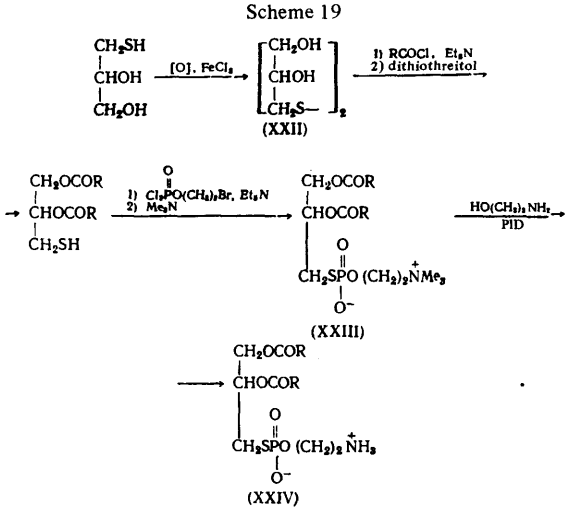
The thioester analogues of PC [compound (XX)] and PE [compound (XXI)] [21] have been obtained from 1-mercapto-*rac*-glycerol[229] by classical methods for the synthesis of PL [230] (Scheme 18):

Scheme 18



In the synthesis of the thio-PL (XXIII) and (XXIV), the temporary protection of the mercapto-group in the acylation of mercaptoglycerol was achieved by oxidising it in air in the presence of iron(III) chloride to the disulphide (XXII) and its subsequent reduction with dithiothreitol[20] (Scheme 19):

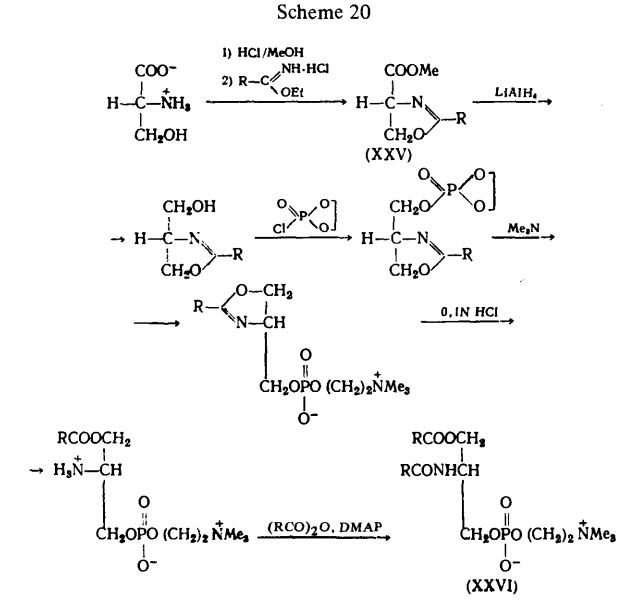
Scheme 19



In the ^{31}P NMR spectra, the chemical shifts of the ^{31}P nuclei in the thio-PL (XXIII) and (XXIV) and in the PL having the natural structure differ by 19 p.p.m.,[43] which makes it possible to observe separately, with the aid of the selective saturation method, the signals of the thio-PL forming part of the composition of liposomal membranes.

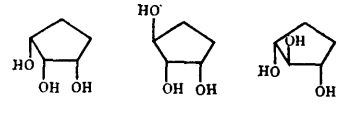
PC analogues non-hydrolysable by phospholipase A_2 have been obtained by replacing the ester linkage in the 2-position in the glycerol residue of PC by the amide linkage. The first synthesis of the acylamide analogue of PC, carried out starting with L-serine,[16,44] led to a racemic compound. Later methods based on the use of D-serine[46] or L-serine[47] were developed and made it possible to obtain the optically active compound. In both cases the key stage of the synthesis is the formation of the oxazoline (XXV) which which makes it possible to reduce the ester group to the hydroxy-group and blocks the amino- and hydroxy-groups in the stages involving the phosphorylation and subsequent alkylation of trimethylamine by the phosphate obtained[46,47] (Scheme 20):

Scheme 20



The amido-PC (XXVI) is a specific inhibitor of phospholipase A_2, exhibiting an even greater affinity for the enzyme than the natural substrate.[46]

PL analogues in which the glycerol residue has been replaced by another triol residue—an alkanetriol (1,2,4-butanetriol[44] or 1,2,5-pentanetriol[48]) or one of the three diastereoisomeric cyclopentane-1,2,3-triols (XXVII)–(XXIX)[49-54]—have been synthesised by traditional methods:



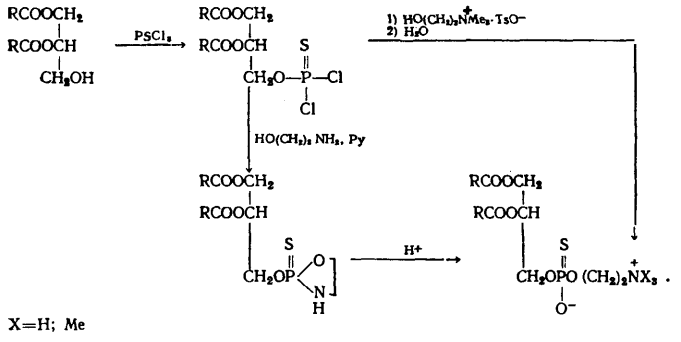
(XXVII) (XXVIII) (XXIX)

5. Synthesis of PL Modified in the Phosphoester Group

The thiono-analogues of PL containing the thiophosphoryl group instead of the phosphoryl group are convenient objects for the study of the behaviour of individual classes of PL in membranes by ^{31}P NMR, since the chemical shifts of the ^{31}P nuclei in thiono-PL and PL having the natural structure differ by 57 p.p.m.,[15,231] which makes it possible to differentiate the thiono-PL using ^{31}P NMR even when these substances are part of the composition of liposomal and biological membranes where the difference in chemical shift reaches 50 p.p.m.[231]

One of the methods for the introduction of the phosphorothioate group into the PL molecule involves the phosphorylation of 1,2-diacyl-*sn*(or *rac*)-glycerol with thiophosphoryl trichloride[62,63] (Scheme 21):

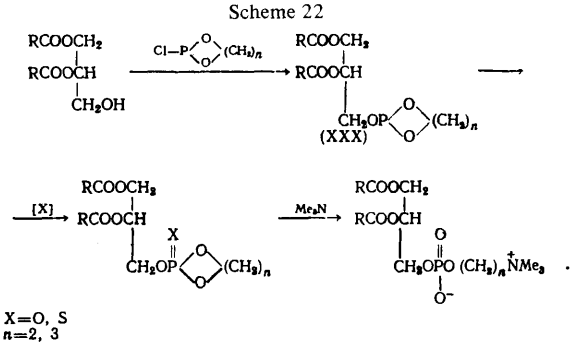
Scheme 21



X=H; Me

Another convenient method of synthesis of thiono-analogues of PC as well as PC analogues with different distances between the P and N atoms involves the oxidation (or sulphurisation) of alkylene phosphites derived from glycerol (XXX) and the subsequent interaction of the cyclic phosphates or phosphonothioates with triethylamine[55,61,232] (Scheme 22):

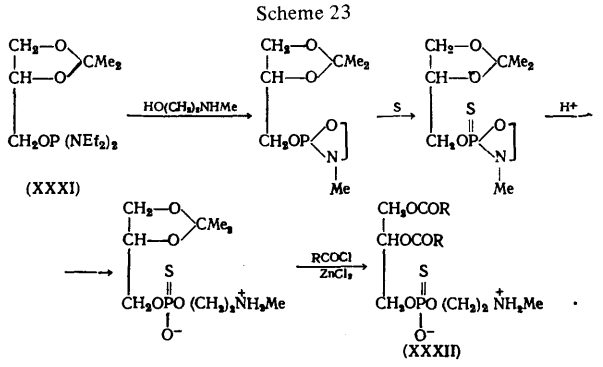
Scheme 22



X=O, S
n=2, 3

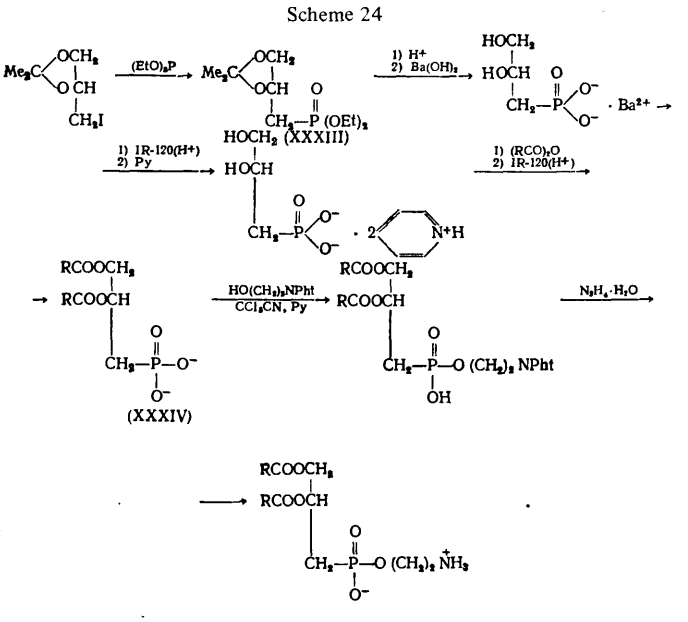
N-Methylthio-PE (XXXII) [60] (Scheme 23), thio-PA,[56,57] and also thiono-analogues of phosphatidylhydroquinones[58,59] have been obtained using various phosphoramidites derived from 1,2-*O*-isopropylidene-*rac*-glycerol (XXXI):

Scheme 23



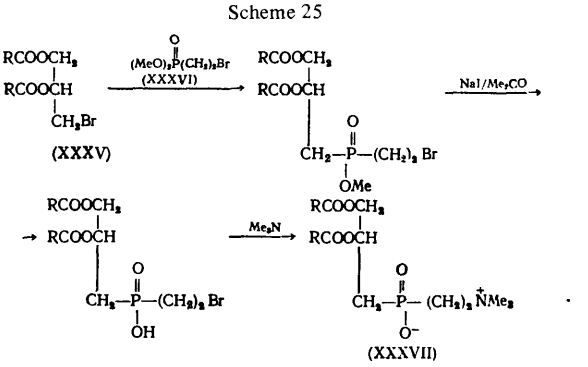
The reaction of the halides of 1,2-disubstituted glycerols with phosphorous acid triesters (Arbuzov alkylation) has been used to synthesise PL analogues in which the polyol is linked to the phosphorus atom by a C–P bond[64,65,67-69] (Scheme 24). The hydrolysis of the resulting diester by the substituted dihydroxypropylphosphonic acid (XXXIII) and subsequent acylation lead to the phosphonic analogue of PA (XXXIV), which can be readily converted into the analogues of other PL [66,67] (Scheme 24):

Scheme 24



The PC analogue (XXXVIII), in which the phosphodiester group has been replaced by the C–P–C linkages (the phosphine analogue of PC), has been obtained by the Arbuzov reaction between the bromohydrin of 1,2-dipalmitoyl-*sn*-glycerol (XXXV) and dimethyl 2-bromoethylphosphonate (XXXVI) with subsequent elimination of the methyl group and quaternisation by reaction with triethylamine[70]‡ (Scheme 25):

Scheme 25

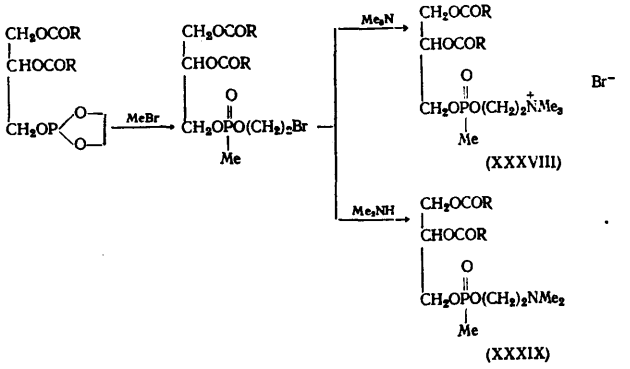


Analogues of PC (XXXVIII) and *NN*-dimethyl-PE (XXXIX), which are neutral esters of methylphosphonic acid, have been obtained by the analogous reaction of ethylene phosphites derived

‡See also Rosenthal.[67]

from 1,2-disubstituted glycerols with methyl bromide[71] (Scheme 26):

Scheme 26



The phosphonic and phosphinic analogues of PL are used as inhibitors of various phospholipases.[16,44]

Thus the modern methods of synthesis of modified PL considered in the review§ make it possible to obtain substances with virtually any structure, necessary both for the study of the structures and functioning of model and biological membranes and for the solution of the ever expanding range of other problems in molecular biology and biochemistry.

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§The methods of synthesis of 2-acetyl-1-alkyl-*sn*-glycero-2-phosphocholine (the thrombocyte activation factor) and its analogous have been described in a review.[233]

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Application of Quantum-chemical Methods to the Diels-Alder Reaction

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The quantum-chemical reactivity indices, used to estimate the relative reactivities of dienes and dienophiles in the Diels-Alder reaction, are analysed and certain problems associated with the use of quantum-chemical methods for the interpretation of cycloaddition selectivity, the reaction mechanism, and the influence of catalysts are discussed.
The bibliography includes 118 references.

CONTENTS

I.	Introduction	397
II.	The use of quantum-chemical indices for the determination of the reactivities of dienes and dienophiles. Allowance for the influence of substituents	398
III.	Predictions based on calculations of the selectivity of the cycloaddition	399
IV.	The mechanism of the Diels-Alder reaction	401
V.	Examples of the study of catalytic reactions	403

I. INTRODUCTION

One of the most interesting reactions in organic chemistry is the Diels–Alder reaction. Many ideas concerning synthesis and profound theoretical concepts, sometimes going beyond the framework of the description of the reaction itself, are associated with it. Wasserman[1] and Woodward and Hoffmann[2] must be regarded as the founders of the theoretical interpretation of the Diels–Alder reaction. Wasserman's kinetic studies showed that the reaction is characterised by a low enthalpy of activation (less than 105 kJ mol^{-1}) and a negative activation entropy which is fairly large in absolute magnitude (on average $\sim$35 e.u.). These estimates lead to the conclusion that, firstly, in the transition state the initial molecules must retain their configuration and, secondly, that the structure of the transition state must resemble the configuration of the adduct formed. Wasserman suggested for the first time that the bond formed between the diene and dienophile arises as a result of the overlap of the molecular π orbitals in the direction of the terminal fragments of the system and not as a result of the lateral overlap of the corresponding *p* orbitals. Woodward and Hoffmann devised the elegant theory of "symmetry allowed" processes, which makes it possible to predict whether or not concerted reactions have a low or high activation energy at an elevated temperature or on exposure to UV light. Reactions for which a low activation energy has been predicted are symmetry-allowed, while reactions with a high activation energy are forbidden. In terms of this classification, the Diels–Alder reaction is a thermally allowed process; on the basis of the ideas described above, it should be regarded as a stereospecific suprafacial process with a concerted synchronous mechanism.

The use of asymmetric reagents, complex and specific dienes and dienophiles, non-standard reaction conditions, and catalysts led very rapidly to the application of this reaction which was popular even without these factors. More profound and detailed experimental studies demonstrated the possibility of also carrying out processes

which are "not allowed" according to the Woodward–Hoffmann hypothesis[3] and also the possibility of a two-stage mechanism,[4,5] in contrast to the classical single-stage synchronous mechanism. New views, showing that even this elegant theory has specific and relative aspects, have appeared.[6]

Many workers have now analysed various aspects of the Diels–Alder reaction. In particular, we may mention reviews in which the reactivity and reaction mechanism,[7–10] the activity and selectivity ratios,[11] the influence of substituents,[9] the regioselectivity and stereoselectivity,[9,11] the symmetry of the transition state,[7] and the possibility of applying perturbation theory[8,9] and frontier orbital theory[10,12] to the description of the characteristic features of the cycloaddition reaction are discussed.

The aim of the present review is the analysis of various quantum-chemical approaches used to investigate the Diels–Alder reaction and also a survey of the characteristic features of this reaction deduced from calculated data.

II. THE USE OF QUANTUM-CHEMICAL INDICES FOR THE DETERMINATION OF THE REACTIVITY OF DIENES AND DIENOPHILES. ALLOWANCE FOR THE INFLUENCE OF SUBSTITUENTS

The first attempts to use quantum-chemical methods for the quantitative description of the reactivities of dienes were based on Brown's hypothesis.[13–18] Its essential feature is the assumption that, in the formation of an adduct, one π electron is localised at each of two terminal carbon atoms of the diene system having a favourable conformation for the addition of the dienophile. Such localisation is a precondition for the formation of two new σ-bonds. The energy necessary for the localisation of two electrons [the *para*-localisation energy (PLE)] was calculated by the LCAO-MO method and was related to the reactivity of the diene—the lower the value of the PLE, the lower the activation energy for the reaction.

PLE has been calculated by the free electron method for polycyclic aromatic hydrocarbons (28 compounds in all).[19] The values obtained were compared with Brown's data. For all the compounds considered, the predictions by the two methods concerning the ability of aromatic hydrocarbons to combine with maleic anhydride generally agree. In certain cases the course of the reaction is influenced significantly by the steric hindrance due to the substituents. For example, according to Brown's calculation, 1,2,3,4-tetraphenylbutadiene should react with maleic anhydride somewhat more slowly than anthracene; in fact the reaction does not occur at all.[18]

In the case of *o*-benzoquinones, the PLE has been used to characterise their dual ability to react as dienes and dienophiles.[20] It was found that these compounds behave as dienes when the *para*-localisation energy is less than a certain value.

For dienes having several possible addition sites, the Diels–Alder reaction proceeds at sites with the lowest value of PLE[20,21] and the highest localisation of charge.[22] The site at which maleic anhydride adds to Klar's hydrocarbon (centrine) has in fact been determined by calculating the PLE.[21]

On the basis of Brown's idea, Sofer et al.[23] introduced various types of indices (ρ) for dienes and dienophiles: indices of the "ethylene", "butadiene", and "benzene" character, which describe the reactivities of the test systems. For the set of polycyclic aromatic structures, the values obtained are compared with the PLE. It has been found that the character of the correlation between ρ and PLE is different for different types of reaction centre. According to Sofer et al.,[23] this permits conclusions about the reaction mechanism. Indices with the "benzene" character ρ_b were used by the same workers to estimate the relative reactivities of different rings in linear polyacenes.[24] It was assumed that $\rho_b = 1$ for benzene; the value of ρ_b is correlated with the PLE, diminishing with increase in the size of the system. The minimum value ($\rho_b = 0.8$) has been obtained analytically for the middle ring in the infinite polyacene; in practice, it is attained when the number of rings is ten.

Epstein[25] used the orders of the bonds between the carbon atoms in the 1- and 2-positions and 3- and 4-positions in the diene as the static reactivity indices. Benzene, 13 polyacenes containing between two and five condensed rings, 10 even polyenes, and 4 heterocyclic systems were considered. It is stated that a correlation was observed between the bond order and the PLE for each type of molecules listed above, but the correlation breaks down when the molecules of different types are considered jointly. This has also been noted by Raghavan and Narasimhan.[20]

Correlations of different reactivity indices should be treated with caution,[26,27] since they depend on the structure of the compounds, i.e. are functions of the "structural variable" s. Within the limits of a given reaction series, two reactivity indices, say A and B, are functions of s: $A(s)$ and $B(s)$. It would seem at first sight that it is sufficient to eliminate the dependence on s and to find the relations $A = A(B)$. However, this cannot be done because s is not a variable in the fundamental sense but depends in its turn on the nature of the substituent. The correlation of the indices is therefore always some kind of approximation.[26,27] It was shown in the same investigation that the correlation of the reactivity indices is impaired when charge transfer takes place in the transition state between the reactants, which is highly characteristic of the Diels–Alder reaction.[7]

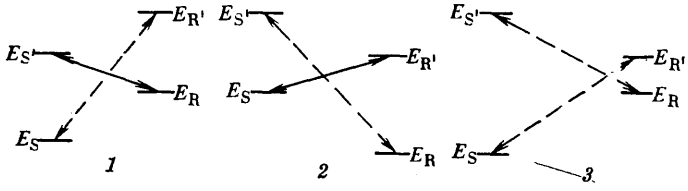
In the PLE, as in other static reactivity indices, no account is taken of the influence of the substituents on the dienophile. Calculation of this kind can then therefore serve only for the description of the relative reactivities of dienes. The change in the π-electron conjugation energy on formation of an adduct from aromatic hydrocarbons has been calculated by the free electron method and related to the relative yields of the reaction products.[28] It was found that a reaction is observed when the losses in the conjugation energy are $< 1.7 \mid \beta \mid$, where β is the resonance integral.

The results of studies on the Diels–Alder reaction involving a series of methyl-substituted 1-ethoxybutadienes (I) and 2-ethoxybutadienes (II) have been analysed.[29] The dienophiles employed were substituted ethylenic compounds $H_2C = CHX$, where X = CHO, CO_2H, $COCH_3$, CO_2CH_3, or CN. Comparison of the experimental data with calculation showed that the logarithms of the rate constants lg k for the reactions considered are linearly correlated with the ionisation potentials of the diene in the series (I) and (II) considered separately. A linear correlation has also been observed between lg k and the electron affinity of the dienophile. The electron density in the frontier MO is also used to account for the reactivity of dienes.[30,31]

We shall consider a series of studies in which account was taken of the influence of substituents.[9,32–35] It is noteworthy that the majority of investigators turn to perturbation theory and to the frontier orbital (FO) approximation in the solution of this problem. Electron-donating substituents increase the energy of both FO's, the energy of the highest occupied molecular orbital E_{HOMO} changing more markedly than the energy of the lowest unoccupied molecular orbital E_{LUMO}. Electron-accepting substituents reduce the energies of both FO's, E_{LUMO} varying more markedly than E_{HOMO}. Depending on the difference between the FO energies of the diene and dienophile, it is formally possible to formulate three types of Diels–Alder reactions: "normal" (*1*), "reverse" (*2*), and "neutral" (*3*) (see Figure).[7,9] The continuous arrow indicates the decisive interaction; such interaction is not observed for reactions of the "neutral" type.

Taking into account the influence of substituents on the FO energy levels in the reactants and the type of decisive interaction, it is possible to predict how these substituents, introduced into the 2π

or 4π system, affect the rate of reaction, since the rate should increase with decrease in the difference between the frontier orbital energies responsible for the interaction.[7,9,32] The theoretical predictions stating that there is a difference between the activation parameters for reactions which obey the forward and reverse Alder rules, that the reactivity of *trans*-disubstituted ethylene, behaving as the dienophile, is higher than that of the *cis*-isomer, and that the introduction of the carbonyl group into the dienophile influences the rate of reaction and predictions concerning the disposition of the orbitals in the reactants, put forward on the basis of calculations by the CNDO/2 method using the perturbation theory, agree with experimental results.[32]



Types of Diels–Alder reactions as a function of the difference between the FO energies of the diene and the dienophile: *1*) "normal" reaction; *2*) "reverse" reaction; *3*) "neutral" reaction; R = diene index; S = dienophile index; E_R, E_S = HOMO energies; E'_R, E'_S = LUMO energies.

The concept of active orbitals has been introduced.[36] Active orbitals comprise the occupied bonding orbital of one of the reactants and the unoccupied antibonding orbital of another. These orbitals describe the bonds formed and broken on cycloaddition. For the "normal" Diels–Alder reaction, the HOMO of the diene and the LUMO of the dienophile are active, whilst the opposite situation obtains for the "reverse" reaction. The experimental activation energy ΔE_{act} obeys the correlation $\Delta E_{act} = \alpha\Delta\varepsilon$, where α is a dimensionless empirical constant for the given reaction (for the Diels–Alder reaction, $\alpha = 0.18$) and $\Delta\varepsilon$ is the difference between the energies of the active orbitals. The quantity $\Delta\varepsilon$ was calculated by the extended Hückel method. The authors[36] believe that the influence of the substituents is associated with the stabilisation and/or destabilisation of the active orbitals.

The influence of electron-donating and electron-accepting substituents on the energies of the HOMO and LUMO of the diene and dienophile has been examined.[37] The rule has been formulated according to which the maximum increase in the rate of the thermal symmetry-allowed cycloaddition reaction of alicyclic reactants is promoted by the introduction of electron-donating substituents into the reactant molecule having the HOMO with the highest energy. This rule is more general than the familiar Alder rule.

It has been shown[38] that the inertness of certain five-membered cyclic chloro-substituted dienophiles in the reaction with cyclopentadiene is associated with the low electron affinities of the test molecules and the low stabilisation energies of the transition state E_s. It has been suggested that there exists a limiting value of E_s, below which the reaction does not occur. The amount of informa-tion contained in certain quantum-chemical reactivity indices of dienophiles was estimated in the same study. The electron affinities calculated by the simple and extended Hückel methods can be useful in the first stage of the study of the reactivity. The reac-tivities of dienophiles in the Diels–Alder reaction are described more adequately by Dewar's MO perturbation method (MOP) and Salem's intermolecular orbital method (IMO). Fukei's frontier orbital method proved unsuitable for the study of compounds of this series. (The frontier orbital approximation cannot be used for heterodienophiles either.[39]) The dependence of the reactivities of dienophiles (ethylenes, benzoquinones, and naphthoquinones) on the nature of the substituents has been considered in a number of studies.[40,41]

The relative reactivities of heterocyclic compounds, namely furan (III), thiophen (IV), and thiophen 1,1-dioxide (V), have been investigated[43] by a modified CNDO/2 method.[42] The stabilising influence of symmetrical (S_π) and antisymmetric (A_π) orbitals of the heteroatom and the SO_2 group on the S_π and A_π MO of the diene and the product was considered as a perturbation of the diene fragment. In furan the 2*p* AO of oxygen have approximately the same stabilising effect on the MO of the product and the reactant and in this case a thermal reaction is possible. The influence of the 3*d* AO of oxygen in furan is insignificant. On the other hand, in thiophen the 3*d* AO of sulphur exert the greatest influence on the A_π MO of the diene, while their influence on the MO of the product is insignificant and the equilibrium in this reaction is strongly displaced towards the reactant. The stabilisation in compound (V) is less marked than in thiophen and the equilibrium is less displaced towards the reactants. The diene reactivity series (IV) < (V) < (III) has been confirmed experimentally.

III. PREDICTIONS BASED ON CALCULATIONS OF THE SELECTIVITY OF THE CYCLOADDITION

The question of selectivity is very important in the Diels–Alder reaction.[9,11] Three types of selectivity are distinguished: chemoselectivity (competition between processes), regioselectivity (competition between the orientations of the reactant leading to positional isomers), and stereoselectivity (competition between the orientations of the reactants leading to geometrical isomers).[44] Special attention is devoted in the literature to the last two types of selectivity. However, competitive processes, for example [2 + 2]-cycloaddition, Michael addition, and the interaction of functional groups, can also arise with the Diels–Alder reaction. The computational method for the prediction of chemoselectivity in the relevant processes has been used very rarely. The chemoselectivity in the reaction of α-dimethylaminostyrene with various dienophiles has been predicted by the MINDO/3 method.[45] Depending on the polarity of the bond in the reactant (the authors introduced a special parameter, equal to the ratio of the difference between the charges on the bonds involved in the multiple bond to its length), one can establish which reaction takes place: [2 + 2]- or [2 + 4]-cycloaddition or the interaction of the amino-group. On the other hand, if several potentially possible Diels–Alder reactions compete, then the more reactive reactants are found to be more selective. This view, derived from the theory of orbital interaction is opposed to the concept put forward previously stating that the less active reactant is the more selective. This means that the processes in which donor–acceptor interactions play a significant role and the relative reactivity is controlled by the frontier orbital energies constitute exceptions to the general rule.[7,12,39] The chemoselectivities and regioselectivities for the radical-cation cycloaddition reactions have been considered.[46]

A general theoretical approach to questions of regioselectivity and stereoselectivity in the Diels–Alder reaction has been described.[9,47–49] Quantum-chemical methods for the determination of the regioselectivity of the process have been used in Refs.50–72 and those for the determination of stereoselectivity have been used in Refs.73–82.

In order to account for the high regiospecificity in the interaction of asymmetric components, the perturbation energies have been calculated by Dewar's method for substituted butadienes (the 1-methyl, 2-methyl, 1-phenyl, and 2-phenyl derivatives) in their reactions with acrylonitrile, methacrylate, and styrene.[50] The coefficients

of the frontier orbitals of the dienes and dienophiles were calculated in terms of the Hückel approximation. The interaction between the atoms of the reacting molecules was taken into account only in the region of bond formation. The calculated perturbation energies for the *o*-, *m*-, and *p*-derivatives were compared with the relative reaction yields. It thus proved possible to predict the preferred orientation in the addition reaction in all the cases examined.

Calculations have been carried out[51] by the PPP method for methyl vinyl ketone and a series of substituted buta-1,3-dienes: 2-methoxy-1-phenylthiobuta-1,3-diene (VI); 2-methoxyphenylthiobuta-1,3-diene (VII); 2-acetoxy-3-(*p*-hydroxyphenylthio)buta-1,3-diene (VIII); 1-acetoxy-4-phenylthiobuta-1,3-diene (IX), and 3-methoxy-3-(2-pyrimidylthio)-buta-1,3-diene (X). The structures of frontier molecular orbitals have been analysed and the regioselectivity in the Diels–Alder reaction has been investigated on the basis of the MOP theory. For all the dienes examined, the transfer of electron density is determined by the primary interaction of their HOMO with the LUMO of the dienophile. The differences between the HOMO coefficients for the corresponding carbon atoms for compounds (VI) and (VII) are small. The regioselectivity of the addition is therefore determined by the character of the LUMO of these compounds, i.e. by the secondary interaction of the LUMO of the diene and the HOMO of the dienophile. The difference between the HOMO coefficients for compound (VIII) is large and the regioselectivity of its addition to methyl vinyl ketone is determined by the primary interaction, in conformity with experimental data. A characteristic feature of 1-acetoxy-4-phenylthiobuta-1,3-diene is that the weak directing effect of the primary interaction is enhanced by the secondary orbital interaction acting in the same direction.

The orientational phenomena in the Diels–Alder reactions of 2R-butadienes with methyl methacrylate have been investigated by the IMO method. A comparison has been made with other methods: the simple perturbation theory and the FO method.[52] The regioselectivity in the reactions of substituted butadienes has also been investigated in other studies.[29,53,54] Analysis within the framework of the perturbation theory in terms of the approximation of F whose coefficients were calculated by the CNDO/S and the Hückel MO method made it possible to account for the regioselectivity in the reactions of methyl-substituted 1- and 2-ethoxybutadienes with substituted ethylenes.[29]

The mode of cycloaddition to various vinylpyridines[55,56] and oxazoles[56] and also of the cyclodimerisation of vinyl pyridines[57] has been correctly predicted and explained on the basis of the formation energies of the regioisomers. If the vinylpyridines function as the dienes, then in their structures it is possible to distinguish formally two pseudodiene fragments: N=C–C=C and C=C–C=C, which must be taken into account in the calculations.[55,57] The formation energies of the regioisomers were estimated in the above studies from

$$\Delta E_\pi = 2\left[\frac{(C_{R_n}C'_{S_m}\beta_{mn} + C_{R_p}C'_{S_q}\beta_{pq})^2}{|E_R - E_{S'}|} + \frac{(C'_{R_n}C_{S_m}\beta_{mn} + C'_{R_p}C_{S_q}\beta_{pq})^2}{|E_{R'} - E_S|}\right],$$

where C and C' are the coefficients of the atomic orbitals of the directly interacting atoms n and p (diene index R) and m and q (dienophile index S) involved in the corresponding HOMO and LUMO, E_R, $E_{R'}$, E_S, and $E_{S'}$ are the frontier orbital energies of the diene and dienophile, and β_{mn} and β_{pq} are the corresponding resonance integrals of the *mn* and *pq* bonds formed in the combined RS system. The coefficients of the AO and the FO energies were calculated by the MINDO/3 method. The experimental data on the stereochemistry of the reaction of 5-ethoxyoxazole with β-acetylacrylic acid and its ethyl ester as well as the reactions of vinylpyridines with azodicarboxylic acid ester and the cyclodimerisation of vinylpyridines agree with the calculations. Similar studies, demonstrating that the observed changes in the reactivity correspond to the stabilisation energies arising as a consequence of the interaction of the frontier orbitals, have been carried out also for the Diels–Alder reaction of the "neutral" type.[58,59]

The π-electon density at the atoms of 5-ethoxyoxazole and acrylic acid and its ethyl ester has been calculated by the Hückel method taking into account the hyperconjugation effects generated by the methyl group. A two-stage mechanism with charge distribution in the transition state has been proposed on the basis of the results of the calculation and the regioisomer formed has been predicted correctly.[60]

The FO theory has been used to account for the isomeric composition of the products of the Diels–Alder reaction.[61] It was postulated that the reaction takes place in two stages and that a weak bond between centres is formed in the first stage. In the special case where the HOMO energy of one molecule and the LUMO energy of the other are close to the energy of the nonbonding orbital, such centres are atoms with the highest, in terms of absolute magnitude, coefficients of the HOMO of the first molecule and LUMO of the second. More than 100 reactions have been investigated within the framework of the Hückel method with various sets of parameters. In all cases the structure of the main product was predicted correctly.

Summarising, one may say that the regioselectivity of the concerted cycloaddition reactions is determined by the orbital effects favouring the formation of bonds between two atoms, to which correspond the coefficients in the expressions for the FO, and between two atoms for which the coefficients for the FO are minimal.[9] On the other hand, Ioffe et al.[62] believe that the relation between the regioselectivity of the reaction and the structure of its transition state is closer and classify the regioselectivity into short-range and long-range components. It follows from the analysis of the structure of the potential energy surface for a reaction leading to two regioisomeric products that the regioselectivity of such a reaction is determined not only by the relative stabilisation of the transition states but also by the height of the ridge separating two valleys on the potential energy surface. If this ridge is low, then a redistribution of the reaction complexes, in conformity with the relative stabilities, can occur during the reaction. In this case the regioselectivity is of the short-range variety and is high when there are significant differences between the stabilisation energies of the transition states. On the other hand, the existence of a high ridge between the valleys prevents the redistribution of the reaction complexes. In other words, in such reactions the regioselectivity is of the long-range kind and is less pronounced, because it is predetermined already in the early stages where the secondary orbital interactions are insignificant.

Ioffe et al.[62] note that, although the calculation of the total potential energy surface is extremely complex, the height of the potential barrier for concerted cycloaddition can be estimated from considerations involving orbital symmetry. On the grounds that the regioisomeric adducts are formed in the Diels–Alder reaction from different transition states and interconversion is difficult, the concerted *supra-supra*-cycloaddition is classified as a process with long-range comparatively low regioselectivity. Different methods of predicting regioselectivities have been compared by Chen.[63]

Quantum-chemical calculations which explain the stereoselectivity in the Diels–Alder reaction have been used for the solution of the problem of both the *endo, exo*-specificity and the *syn, anti*-specificity. On the basis of experimental data obtained in the study of the reaction of cyclopentadiene with maleic anhydride, Alder and Stein concluded that differential *endo*-orientation obtains and explained it by the "maximum accumulation of unsaturation".[1] Woodward and Hoffmann[2] explained this rule by the fact that the FO of the secondary centres, i.e. atoms which are not linked to one another in the adduct (the interaction of the orbitals of the secondary centres is

referred to as secondary orbital interaction), may overlap for the *endo*-adduct. This electronic effect lowers the activation energy for the reaction and hence the *endo*-adduct is formed faster. The study of the reaction of cyclopentadiene with various dienophiles within the framework of the Hückel method showed that the delocalisation energy of the *endo*-configuration is always greater than that of the *exo*-isomer,[73,74] which conforms to the Alder–Stein rule. A model calculation for the coplanar *endo*-oriented complex in the reactions of cyclopentadiene with acrolein, crotonaldehyde, butadiene, isoprene, and piperylene has been carried out by the Hückel method including Madelung's correction to the energy.[75] The distance between the plane of the diene and the dienophile was varied in the range 2.6–4.0 Å. It was found that in the range investigated the *endo*-orientation is always energetically more favourable than the *exo*-orientation and that the charge transfer from the diene to the dienophile in the case of the *endo*-orientation exceeds that for the *exo*-orientation.

However, experimental data have shown that the Alder–Stein rule is not absolute. A mixture of isomers is usually formed, their ratio depending on the nature of the initial compounds, the electronic and steric effects, and also the reaction conditions. Under conditions of thermodynamic control, there is a possibility of the preferential formation of the more stable *exo*-adduct. Such uncertainty in the prediction of the expected stereoisomer can be explained by the fact that the secondary orbital interactions responsible for the stereoselectivity have low energies and the influence of other factors is therefore extremely important. For this reason, in contrast to the problem of the regiospecificity of the Diels–Alder reaction, it is much more difficult to solve the problem of the stereoselectivity by computational methods.

Mazzoechi et al.[76] investigated the π-surface stereoselectivity of the cycloaddition of hexachlorocyclopentadiene to 7R-norbornadienes (R = H, t-BuO, $PhCO_2$, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Ph, *p*-FC_6H_4, Cl, CH_3CO_2, or Me). Non-empirical *ab initio* MO calculations have shown that the substituents in the 7-position influence the reorientation of the π-bonds in space, the ease of the displacement of the olefinic protons from the plane, and probably the very planarity of alkenes. The substituents investigated increase the electron density at one of the two bonds of the ring. The dependence of the partial reaction rate factors on the electronegativity ε of the substituent *R* can be satisfactorily explained for *anti, exo*-attack. In the case of *syn, endo*-attack, a significant acceleration of the latter has been demonstrated for 7-t-butoxynorbornadiene. However, the slight variation of the partial rate factor as a function of ε for *syn, endo*- and *anti, endo*-attack could not be fully explained.

In a study of the stereochemistry of cycloaddition to substituted acetylenic and ethylenic compounds,[77] it was found that a dienophile adds stereospecifically to the endocyclic diene fragment of fulvenes from the side opposite the CH_2 bridge. In order to explain this phenomenon, calculations were carried out by the MINDO/3 and INDO methods. On the basis of the perturbation theory, the authors[77] believe that such stereospecificity of the cycloaddition is caused by the fact that, when the dienophile is attacked from the side of the methylene bridge, a strong antibonding interaction takes place between the HOMO of the dienophile and the LUMO of the diene (especially in the *exo*-oriented transition state), because the π orbitals of the terminal atoms of the diene are turned inwards towards the π orbitals of the dienophile. On the other hand, one must take into account the fact that the four-electron four-centre interaction considered weakens under the conditions of the *endo*-attack, since the corresponding π orbitals of the diene fragments are turned away from the dienophile. Analysis of the calculated data and photoeletron spectra also permits conclusions concerning the role of the σ–π interactions of the orbitals in the test systems.

In order to account for the experimental observation of the formation of the *exo* or *endo*-configuration with the *syn*-position of the nitrile group in the reactions of cyclopropenes with various dienophiles, the qualitative perturbation theory has been used.[78] The authors based their conclusions on the fact that the steric structure of the transition state is determined by the maximum overlap of the frontier MO of the adducts.

The study by the INDO method of the influence of the methyl groups on the rate and stereochemistry of the cycloaddition and the use of kinetic data for a series of tricyclo[5.2.1.$0^{2,6}$]decadienes and trienes[34] showed that electronic effects play the main role in determining the selectivity (for the majority of compounds). It is believed[34] that one of the main factors determining the reaction selectivity is the character of the distortion of the MO. For norbornyl-condensed spirocyclic cyclopentadiene systems, the mixing of the σ and π orbitals of the dienes plays the most significant role. It is responsible for minimising the antibonding interactions for the observed stereochemistry of the cycloaddition, which has been demonstrated with the aid of the INDO method.[79] The *syn,anti*-stereoselectivity has been investigated as a function of the geometry of the transition state.[80]

The factors influencing the stereoselectivity of the cycloaddition reactions have been examined in a review.[81] It was concluded that the stereoselectivity is determined mainly by the orbital interaction. The application of perturbation theory to the determination of the selectivity of processes has been discussed in detail in a number of studies.[9,83,84]

IV. THE MECHANISM OF THE DIELS–ALDER REACTION

For a long time, the Diels–Alder reaction was assumed to be a concerted suprafacial process with a single-stage synchronous mechanism. This idea was based on the Woodward–Hoffmann theory of orbital symmetry. However, certain experimental and calculated data obtained in recent years make it necessary to consider the following question: is the classical mechanism in the Diels–Alder reaction the rule or an exception. On the basis of the results of kinetic studies by Dewar,[4] one may conclude that the transition state is asymmetric in the reactions of furan derivatives with maleic anhydride. According to the results of the same worker, obtained by the MINDO/3 and MNDO methods, any synchronous processes involving the participation of more than one bond have unduly large activation energies and therefore can hardly occur.[5] Our experimental studies on isoindoles also confirm the possibility of non-synchronous cycloaddition.[85,86]

Nevertheless, from our point of view, the complete neglect of the orbital symmetry theory is unjustified at the present stage. This theory has provided too many explanations for organic chemists to be abandoned without adequate justification. In the general case one must therefore take into account the possibility of both a many-centre synchronous mechanism and a two-stage mechanism with the intermediate formation of a zwitterion or a biradical. A concerted but non-synchronous mechanism, i.e. one where two new bonds are formed at different rates, is also theoretically feasible.

The structure of the transition state of the reaction depends on the proposed mechanism. In the theoretical analysis of this process with the aid of MO methods, one must therefore use different approaches.[87]

Quantum-chemical calculations have been applied most often to the study of the mechanism of the cycloaddition of ethylene to butadiene. It has been demonstrated by the CNDO/2 method that the approach of the ethylene molecule from "above" and not from the plane of butadiene is most favourable.[88] The reaction takes place in such a way that the principle of the maximum overlap of the $2p_\pi$ orbitals of ethylene and the analogous orbitals of the

terminal carbon atoms of butadiene is obeyed. Significant changes in the structure of the reacting molecules, in bond lengths, and in the hybridisation of the atoms take place only when the distance between the carbon atoms of the ethylene and the terminal carbon atoms of butadiene is less than 2 Å. It has been noted that the $\sigma-\pi$ interaction plays a significant role in estimations of the energy characteristics of the reaction. In the case of substituted ethylenes and butadienes,[82] the $\sigma-\pi$ interaction is also very important as a factor controlling the selectivity of the addition.

It has been observed[74] that the stability of the complexes formed between the *cis*-butadiene and dienophile (ethylene or *p*-benzoquinone) components is low if the distance between the components is ~3.0 Å. The stabilisation energy of the charge-transfer complexes in the reaction with ethylene is 16.76 kJ mol^{-1} and that for the reaction with benzoquinone is 37.71 kJ mole^{-1}. It has been noted[88,89] that charge transfer takes place from butadiene to ethylene in the course of the formation of the activated complex. It has been demonstrated[90] that, in the analysis of the dependence of the rate of reaction on the nature of the dienophile, it is likewise necessary to take into account the charge transfer between the components of the diene synthesis.

The non-empirical method for the calculation of the reaction pathway in the cycloaddition of ethylene to butadiene within the framework of the Roothaan method makes it possible to establish that during the reaction the planes of the molecules are disposed at an angle of 70° relative to one another.[89] In the same study an attempt was made to determine the heat of reaction and to estimate the electronic and geometrical structures of the transition state. However, it was found that an unsuccessful method had been used for the optimisation of the geometrical parameters.[91]

An interesting method has been proposed[92] for the description of the reactivity (including that in the Diels–Alder reaction), in which the state of each atom involved in the reaction is described by a parameter called the reaction angle. Two computational schemes, based on the PPP and Hückel MO approximations have been developed. The first has been called the method of topological molecular orbitals (TMO) with configuration interaction (TMO-CI) and the second TMO scheme is a simplified version of the first in which the intermolecular repulsion integrals were disregarded. The total energy of the system is described as a function of the reaction angles. This function describes a topological hypersurface; the reaction mechanisms are discussed in terms of stationary points on the hypersurface. A detailed analysis has been carried out for the reaction of butadiene with ethylene.[92] Minima corresponding to the reactants and products (cyclohexene) and two saddle points, corresponding to the *supra, supra-* and supra, antara-cycloadditions were found on the hypersurface for this reaction. However, only the former corresponds to the true activated complex (the gradient at this point is zero and the Hess matrix has only one negative eigenvalue). The activation energy for the reaction, amounting to 101 kJ mol^{-1} (Hückel MO) and 112 kJ mol^{-1} (PPP), was calculated for the *supra, supra*-cycloaddition. An additional saddle point corresponds to the singlet biradical, but the reaction pathway, linking the reactants to this biradical, passes through a stationary point at which Hess's matrix has two negative eigenvalues. The two stage mechanism is therefore prohibited owing to infringement of the Murrell–Laidler rules. On the other hand, the biradical can be obtained from the reaction products. This is a possible mechanism in cases where the stereoselectivity of the reaction diminishes.

The biradical transition state of the Diels–Alder retroreaction cyclohexene → butadiene + ethylene is supported by the results of the study of the fragments of the potential energy surface carried out in terms of the MINDO/3 approximation with full optimisation of the geometry.[93] The calculations were performed taking into account the configuration interaction. The transition state found was consistent with an asymmetric biradical to which corresponds an activation energy of 428.9 kJ mol^{-1} (experimental value 268.8 kJ mol^{-1}). According to the author,[93] the unrestricted SCF method provides a more correct description of potential energy surfaces, making it possible to distinguish two stages in the retroreaction investigated: the first, rate-limiting stage involving the formation of an asymmetric biradical intermediate with an activation energy of 365.4 kJ mol^{-1} and the second stage involving the decomposition of the intermediate to ethylene and butadiene with an activation energy of 79.9 kJ mol^{-1}. The activation entropies for the first and second stages as well as the kinetic isotope effects were calculated and it was concluded that the latter cannot serve as a criterion for the choice between the synchronous and non-synchronous mechanisms of the Diels–Alder reaction.

Bazilevskii[26] and Tikhomirov[27] suggested that corrections be introduced into the semiempirical π-electron PPP theory in order to take into account the non-orthogonality of the basis AO and the electronic correlation. The correction for the non-orthogonality (exchange repulsion) together with allowance for the Coulombic interaction of the atoms leads to the appearance of a new contribution in the expression for the energy of the system. The potential surface for the Diels–Alder reaction in the ethylene–butadiene system is constructed taking into account this contribution and using the hybrid orbitals. It has been noted that, for a fixed method of calculation of the energy taking into account an incomplete set of degrees of freedom (which is frequently done), one can obtain only the upper limit to the activation barrier (because the crossing point is an extremum).

The results of calculations of the energy of π electrons in terms of the PPP approximation established that the pathway involving the consecutive formation of σ-bonds requires a higher activation energy.[94] The reaction of butadiene with ethylene has been investigated also in other studies,[95–98] whose results do not conflict with these ideas. The possibility of a single-stage mechanism with a pericyclic transition state and of a two-stage mechanism with the intermediate formation of a biradical has been discussed.[99]

Thus one may conclude that the results of quantum-chemical calculations for the forward Diels–Alder reaction between butadiene and ethylene indicate a single-stage synchronous mechanism with the intermediate formation of a charge-transfer complex. However, the retroreaction is characterised by a two-stage mechanism with the intermediate formation of a biradical (or by a single-stage mechanism with a biradical transition state).

A number of studies have been devoted to the mechanism of the reactions of substituted butadienes and ethylenes. The parameters of the transition states for the Diels–Alder reactions of 1- and 2-ethoxybutadienes with acrolein have been calculated by the MINDO/2 method for two reaction mechanisms: the concerted synchronous mechanism and a non-synchronous mechanism.[98] The geometrical parameters were optimised by minimising the energy using Rinaldi's method. The calculated potential barriers to the reaction led to the conclusion that 2-ethoxybutadiene reacts preferentially via the concerted mechanism, while 1-ethoxybutadiene reacts via a non-synchronous mechanism. The calculated activation energies (163 and 119.5 kJ mol^{-1} respectively) agree with the observed rate constants for the reactions of these isomers with acrolein at 65 °C.[98] Evidence supporting the single-stage mechanism for substituted butadienes has also been obtained in other studies.[29,100]

Calculations for the transition state[101] in a reaction involving the cyclodimerisation of buta-1,3-diene to 4-vinylcyclohexene by various methods, (FO, MINDO/3 and *ab initio* SCF MO) showed that the activation energy is reduced when a radical-cation is formed as an intermediate, which is inconsistent with the synchronous mechanism. The authors[101] suggest that the Diels–Alder reaction between

buta-1,3-diene and the butadiene cation proceeds in accordance with a concerted but non-synchronous mechanism via a bisallyl radical-cation in which the pericyclic interaction is relatively weak.

We shall now return to the study mentioned previously[29] in which the mechanism of the reaction of ethoxybutadienes with various dienophiles is discussed (see above). The calculations were performed within the framework of the perturbation theory in terms of the FO approximation and the frontier orbital coefficients were calculated by the CNDO/S and the Hückel MO methods. Comparison of the calculated interaction energies of the frontier orbitals with the logarithm of the reaction rate constant with the aid of correlation analysis leads to the conclusion that a synchronous mechanism operates in the series of compounds II and a non-synchronous mechanism in the series of compounds I. However, the CNDO/S and Hückel MO methods yield opposite answers to the question as to which of the two bonds is formed earlier.

An interesting approach to the study of the reaction mechanism has been proposed.[102] On the basis of the FO theory, the role of the donor–acceptor interaction in two systems is considered qualitatively: (1) with the diene as the donor and the dienophile as the acceptor; (2) with the dienophile as the donor and the diene as the acceptor. The objects of study are not specified exactly. It follows from the analysis in the above investigation[102] that the simultaneous formation of two bonds is possible if the interaction between antisymmetric MO predominates. On the other hand if the interaction between symmetrical MO is decisive, the probability of the formation of a cyclic transition state diminishes.

In relation to the interaction of cyclopentadiene with various dienophiles and of maleic anhydride with various dienes, it has been shown[74] that the diene and the dienophile are charged positively and negatively respectively in the intermediate complex. The degree of polarisation is correlated with the delocalisation energy of the corresponding complex, which is linearly related to Brown's *para*-localisation energy.[74]

The distribution of electron density in the π-complexes between the diene and the dienophile, which have been identified with the activated complexes in the Diels–Alder reaction to simplify the procedure, has been studied with the aid of a modified version of the Hückel method.[103] The π-complexes of cyclopentadiene with ethylene, acroleine, *p*-benzoquinone, and 1,4-naphthoquinone and the π-complexes of maleic anhydride with benzene, napthalene, anthracene, phenanthrene, pyrene, benzanthracene, dibenzanthacene, benzophenanthrene, pentacene, and hexacene were examined. The distance between the molecular planes was assumed to be 1.87 Å. The resonance integrals arising when the molecular interaction was considered were assumed to be proportional to the overlap integrals. In all the π complexes investigated, the diene component is the electron donor. The magnitude of the transferred charge increases with increasing delocalisation of the π complex. It was found that the degree of conjugation in the π complexes corresponding to the endothermic reactions is greater than in the π complexes in the exothermic reactions.

The reactivity of dienophiles having different structures in their reactions with cyclopentadiene has been investigated by the method of intermolecular orbitals (IMO) using a coplanar model of the transition state (TS).[104] Such calculation presupposes the equality of the overlap integrals between different atoms. The interaction energy E_{in}, equal to the stabilisation energy, is used as a characteristic of the of the reactivity for various kinds of mutual approach of the molecules. Within the limits of three reaction series of dienophiles (A—cyanoethylenes, B—maleic anhydride derivatives, C—quinones), the values of E_{in} were calculated for two types of coplanar TS: *endo* and *exo*. It was shown that the IMO method is applicable to the description of the reactivities of symmetrical dienophiles (series B and C), and leads to unsatisfactory results for asymmetrical dienophiles (series A). The authors[104] therefore suggest that the IMO-2 method, in which it is assumed that the primary overlap integrals are not equal, be used. The E_{in} surface, plotted in terms of the coordinates of the overlap integrals, has a saddle point at the origin of coordinates. On the basis of this approach (IMO-2), the authors introduced a new reactivity index, equal to the maximum positive curvature of the interaction energy surface (f_{max}), whose value is independent of hypotheses concerning the structure of the transition state (the TS can be non-coplanar). In the same study, it was also shown that in many instances the index f_{max} contains more information than E_{in}. In particular, the use of this index makes it possible to describe satisfactorily both symmetrical and antisymmetric TS (for example in the reactions of cyclopentadiene with series A dienophiles).

The transition states in the reactions of butadiene with ethylene, cyclopropene, and cyclopropenone have been investigated by the IMO-2 method.[94] The molecular geometry was assumed to be unchanged during the reaction. Variation of the geometrical parameters characterising the mutual disposition of the molecules and the structure of different sections of the potential surface for the reaction led to the conclusion that the non-coplanar mutual approach of the molecule is preferred. It was shown that the molecular planes of the diene and the dienophile in the TS are disposed at an angle whose value is intermediate between the angles in the coplanar model and in the adducts. The use of the IMO-2 method also leads to more correct results in the study of the reactivity of the dienophiles, of the *endo*/*exo* ratio for the products, and of other features of the Diels–Alder reaction.

The calculation of the stabilisation energy of the transition state has been used to characterise the reactivity.[105] The application of the extended Hückel method to the determination of the TS energies in the reaction of maleic anhydride with cyclopentadiene yields a correct view of the relative reaction rates, in agreement with experimental data.

Calculations have been performed[106] for the π-complexes of maleic anhydride with various polycyclic aromatic compounds (32 structures in all). The complex of maleic anhydride with naphthalene was chosen as the model. It was shown that the overlap integral $2p_\pi$–AO for σ interactions passes through a maximum with decrease in the distance R between the diene and the dienophile, which corresponds to a minimum on the potential curve for the two π-systems. The value of R corresponding to the minimum potential energy (R_0) depends on the effective charges at the ends of the diene system of the polycyclic hydrocarbon. It has been suggested that the formation of the π-complex determines the rate of the diene synthesis. For many of the systems considered, the delocalisation energy of the π-complexes is correlated with the PLE.

The stabilisation energy of the transition state has been calculated also in other studies.[31,107,108] The influence of energetic, geometrical, and electronic characteristics on the cycloaddition mechanism has been discussed.[109] The mechanisms of cycloaddition have been described in terms of orbital symmetry.[110–114]

V. EXAMPLES OF THE STUDY OF CATALYTIC REACTIONS

Computational methods have also been applied to the study of catalytic Diels–Alder reactions.[30,44,57,98,99] It has been noted[51] that catalysis by Lewis acid diminishes the role of the secondary orbital interaction involving participation of the LUMO of the diene, which reduces the selectivity of the reactions of methyl vinyl ketone with thio-derivatives of buta-1,3-diene. The experimental data on the regioselectivity of the thermal and catalytic addition of 2-methoxy-1-phenylthio- and 2-methoxy-3-phenylthio-buta-1,3-dienes confirm this conclusion. The boundary electron densities of isoquinolinequinone and of its complexes with BF_3 and acids have been calculated by the

MNDO method; the regioselectivity in the Diels–Alder reaction with asymmetric dienophiles has been predicted.[115]

It has been noted[69] that protonation reduces the LUMO energy of acrolein, which should increase the interaction energy of the frontier orbitals and increase the rate of reaction. Furthermore, the reaction of acid catalysts increases the difference between the LUMO coefficients of the corresponding carbon atoms, which increases the process selectivity, since the latter becomes more marked with increasing difference between these coefficients (other conditions being equal).

The potential barriers and the charge distribution have been calculated by the MINDO/3 method for the Diels–Alder reaction between 1-hydroxybutadiene and acrolein and a study has been made of the influence of catalysts on this reaction.[108] In the case of a non-catalytic reaction, the activation energies for *o*-endo-, *o*-exo-*m*-endo-, and *m*-exo-additions are respectively (in kJ mol^{-1}) 124.15, 124.28, 205.6 and 207.74. In the presence of BF_3 and NH_4^+, the activation energy for the *m*-addition decreases slightly (by 25 to 42 kJ mol^{-1}), whereas the activation energies for the *o-endo-* and *o-exo*-additions are respectively 62.77 and 64.57 (in the presence of BF_3) and 46.93 and 52.04 (in the presence of NH_4^+). These data explain the experimentally observed influence of Lewis acids on regioselectivity and stereoselectivity. The transition state corresponds to the most pronounced charge transfer from the diene to the dienophile and from the reactants to the catalysts. Other studies have also been devoted to the regioselectivity and stereoselectivity in catalytic Diels–Alder reactions.[117,118]

It is noteworthy that calculations for the catalytic cycloaddition reactions are undoubtedly more complex and that a correlation between the presence of a catalyst and change in process selectivity does not always occur.

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Metal-carboxylic Acids and Their Derivatives

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Questions connected with the synthesis of metal-carboxylic acids, compounds incorporating [M] -COOH fragments with a metal-carbon bond in which M is a transition metal complex, and their derivatives (salts, esters, and amides) are considered. The bibliography includes 189 references.

CONTENTS

I. Introduction 406
II. Metal-carboxylic acids 407
III. Metal-carboxylic acid salts and polynuclear transition metal complexes of carbon dioxide 410
IV. Esters of metal-carboxylic acids (alkoxycarbonyl complexes of transition metals) 410
V. Amides of metal-carboxylic acids (carbamoyl complexes of transition metals) 412

I. INTRODUCTION

Metal-carboxylic acids (MCA) [M]−COOH constitute a new type of organometallic compound. The interest in complexes of this type is associated with studies on the formation of complexes by carbon dioxide with transition metal compounds.[1-7] The formation of MCA and their derivatives is also encountered in the study of various reactions in the presence of transition metal complexes. A review on MCA and their derivatives appeared in 1972.[8]

In the present review, covering the literature up to 1985, attention has been concentrated on the preparation of MCA and their derivatives and the literature on catalytic processes with the intermediate formation of [M]−COOH, [M]−COOR, or [M]−$CONR_2$ groups is covered only fragmentarily. The review also hardly reflects data on the synthesis of unstable MCA esters and amides by the usual methods.

The formation of MCA and their derivatives (esters and amides) in intermediates has been postulated in various catalytic processes with participation of carbon monoxide and carbon dioxide, although their involvement in the catalytic step has not been rigorously demonstrated. At any rate, one of the possible pathways in the majority of these processes may involve the intermediate formation of [M]−COOH, [M]−COOR, or [M]−$CONR_2$. The synthesis of higher carboxylic acids and their esters from unsaturated compounds, carbon monoxide, and an alcohol (or water) in the presence of transition metal compounds (the Reppe synthesis) can also be assigned to reactions of this type:[9-15]

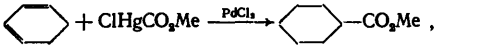
$$H_2O + [M] \rightleftarrows H[M]OH ,$$
$$H[M]OH + CO \rightleftarrows H[M]CO_2H ,$$
$$H[M]CO_2H + \underset{|\ |}{\overset{|\ |}{C{=}C}} \rightarrow \underset{|\ |}{\overset{|\ |}{HC{-}CCO_2H}} + [M] ,$$
$$\text{or } H[M]OR + CO \rightleftarrows H[M]COOR ,$$
$$H[M]COOR + \underset{|\ |}{\overset{|\ |}{C{=}C}} \rightleftarrows \underset{|\ |}{\overset{|\ |}{HC{-}CCOOR}} + [M] ,$$

where [M] is a fragment of the transition metal complex.

The formation of MCA esters as intermediates has been put forward also in the reaction involving the carbonylation of alkyl halides by carbon monoxide in the presence of transition metal complexes (see Fracalanci et al.[16] and the literature quoted therein). Although the metal-carboxylic acid can be isolated in a pure state from the reaction mixture under the conditions of the reaction involving the addition of formic acid and its esters to unsaturated compounds,[1,17] the question of the character of the transfer of the carboxy-group to the olefin with formation of H[M]COOH remains open; one of the possible pathways is as follows:

$$HCO_2H + [M] \rightarrow H[M]CO_2H ,$$
$$H[M]CO_2H + \underset{|\ |}{\overset{|\ |}{C{=}C}} \rightarrow \underset{|\ |}{\overset{|\ |}{HC{-}CCO_2H}} + [M] .$$

It is entirely possible that the esters of palladium-carboxylic acid are formed as intermediates in the carboxylation of unsaturated compounds in the presence of palladium salts[18] and in the synthesis of oxalic and carbonic acid esters by the reaction of carbon monoxide with alcohols:[19-21]



$$2CO + 2ROH \xrightarrow{PdCl_2} RCO_2CO_2R .$$

One cannot rule out the possibility that the electrocatalytic carboxylation of olefins in alcohols in the presence of platinum complexes proceeds, as postulated by Inoue and Tsutsumi,[22] with formation of a platinum-carboxylic acid ester, while the electro-chemical reduction of carbon dioxide at a platinum electrode results in the formation of the $[Pt]CO_2H$ fragment.[23] A reaction mechanism involving stages with participation of metal-carboxylic acids has been proposed for the electrocatalytic reduction of CO_2 to carbon monoxide in the presence of cobalt and nickel complexes:[24]

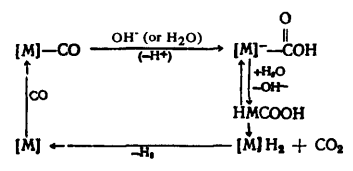
$$[LM^{III}CO_2Na]^{n+} + H_2O \overset{fast}{\rightleftarrows} [LM^{III}CO_2H]^{n+} + NaOH ,$$
$$[LM^{III}CO_2H]^{n+} + e \rightarrow [LM^{II}CO_2H]^{(n-1)+} ,$$
$$[LM^{II}CO_2H]^{(n-1)+} \xrightarrow{slow} [LM^{II}]^{n+} + CO + OH^- .$$

where M is the metal and L an N-containing ligand.

In connection with this study, one should note that much attention has been devoted recently to the investigation of the reactions involving the oxidation of CO by water in the presence of transition metal complexes:[25-32]

$$CO_2 + H_2O \overset{[M]}{\rightleftarrows} H_2 + CO_2 .$$

This reaction takes place via a general mechanism involving as one of the stages the formation of an unstable metal-carboxylic acid[31] (see also Vol'pin and Kolomnikov[25] and the literature quoted therein):



There is no doubt that metal-carboxylic acids or their esters are formed in all the reactions quoted above, although the transfer of the carboxy-group to the olefin remains in many respects obscure. Therefore the synthesis and study of the properties of metal-carboxylic acids and their derivatives will promote in many ways the elucidation of this complex process.

A fair amount of attention has also been devoted in the literature to the synthesis of carbamoyl compounds of transition metals (metal-carboxylic acid amides), which are intermediates in catalytic processes.[8] The synthesis of metal-carboxylic amides and the study of their properties are of undoubted interest for the understanding of the mechanism of carbonylation of amines in the presence of transition metal complexes.[33,34]

To conclude this, by no means complete, list of reactions in which the formation of metal-carboxylic acids and their derivatives as intermediates plays a major role, one must emphasise the importance of the chemistry of these compounds, because they constitute an independent class of organometallic compounds. Syntheses based on them extend the possibilities of coordination and organometallic chemistry. On the other hand, platinum(or gold)-carboxylic acids and their derivatives can be of interest from the practical point of view as antitumour medicinal preparations.[35]

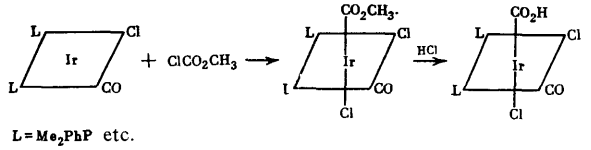
II. METAL-CARBOXYLIC ACIDS

1. Stable Metal-carboxylic Acids

Although the intermediate formation of MCA is frequently postulated, their preparation in a pure state involves considerable difficulties. The number of stable metal-carboxylic acids described in the literature is small. The synthesis of such acids would make it possible to obtain their various derivatives by analogy with the chemistry of carboxylic acids. On the other hand, as already mentioned above, metal-carboxylic acids are of great interest for preparative coordination chemistry, because specific synthesis of transition metal complexes with carbon dioxide via the following pathways is possible with their aid:

$$[M]OH + [M']CO_2H \rightarrow [M']CO_2[M] + H_2O\ ,$$
$$[M]HCO_3\ (\text{or}\ [M]_2CO_3) + [M']CO_2H \rightarrow [M']CO_2[M] + CO_2 + H_2O\ .$$

A stable metal-carboxylic acid was first described in 1969:[36]



L = Me_2PhP etc.

According to the data of these workers, the iridium-carboxylic acid is formed as colourless crystals stable in air. The IR spectrum of the resulting compound contains the intense ν(CO) = 1663 cm^{-1} (KBr) absorption band as well as the distinct ν(OH) = 3313 cm^{-1} (dry deuteriochloroform) absorption band. Titration of the iridium-carboxylic acid in aqueous acetone after the addition of one equivalent of alkali led to the observation of the evolution of carbon dioxide and the formation of the initial complex $L_2Ir(CO)Cl$. Carbon dioxide is also evolved on thermolysis of the acid with formation of the iridium hydride complex $L_2Ir(CO)HCl_2$.

The question of the formation of an iridium-carboxylic acid on hydrolysis of the complex $L_2Ir(CO)Cl_2(COOCH_3)$ has been investigated using the methods proposed by Deeming and Shaw;[36] when gaseous HCl is passed through a benzene solution of the iridium-carboxylic acid ester, only a mixture of the acid with the initial ester can be isolated from the reaction mixture in all cases.[37] The lack of information about this acid in later literature is probably associated with this finding.

Iridium-carboxylic acids of the above type have also been obtained on treating phosphine complexes of tervalent iridium with formic acid.[38] However, in view of the insignificant yields of the acids, this procedure cannot be regarded as preparative.

The preparation of a platinum-carboxylic acid via the mechanism

$$\text{dppe}\,Pt(R)OH + CO \rightarrow \text{dppe}\,Pt(R)CO_2H$$
$$R = Me,\ C_6H_5;\ \text{dppe} = Ph_2PCH_2CH_2PPh_2$$

has been reported.[39] However, this communication contains no data on IR spectroscopy, elemental analysis, etc. Analogous platinum-carboxylic acids were obtained later: $(Ph_2PCH=CHPPh_2)Pt(CO_2H).(CH_3CN)$ with m.p. 177–179 °C [ν(OCO) = 1604 cm^{-1} (v.s.) and ν(OH) = 2680 cm^{-1} (v.w.)] and $(Ph_2PCH=CHPPh_2)Pt(CO_2H).(CH_3CF_3)$ with m.p. 188–190 °C [ν(OCO) = 1610 cm^{-1} (v.s.) and ν(OH) = 2685 cm^{-1} (v.w.)].[40] The platinum-carboxylic acid *trans*-$(Et_3P)_2Pt(CO_2H)Cl$, which is unstable in air, has been obtained recently by treating the cationic complex $[(Et_3P)_2Pt(Cl)CO][BF_4]$ with water;[41] the IR spectrum contains the ν(OCO) = 1595 cm^{-1} (v.s.) and 1150 (s.) as well as the ν(OH) = 3140 cm^{-1} (v.w.) absorption bands; the last band shifts to ν(OD) = 2240 cm^{-1} (v.w.) when hydrogen is replaced by deuterium. According to NMR data, the spin–spin coupling constant $J^{195}_{Pt-^{13}C}$ = 1337. It is noteworthy that this method of synthesis of metal-carboxylic acid is the easiest among all those available.

The comparatively stable rhenium-carboxylic acid of the type η^5-CpRe(CO)(NO)COOH has been obtained by treating the cationic complex $[\eta^5\text{-CpRe(CO)NO}]^+$ with aqueous solutions of triethylamine or alkali.[42–44]

The rhenium-carboxylic acid is quantitatively converted into the hydride complex CpRe(CO)(NO)H in absolute tetrahydrofuran (THF). The IR spectrum of the acid in THF contains the 2960 (s., br.) and 1631 (m.) absorption bands, while the ^1H NMR ($CDCl_3$) spectrum contains the δ = 9.47 p.p.m. signal. According to Sweet and Graham,[43] the interaction of a dialkylamine with the rhenium-carboxylic acid in solution results in the formation of the metal complex of carbon dioxide:

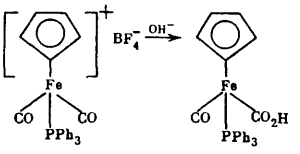
$$[Re]COOH + R_2NH \rightarrow [Re]COO^- \ldots H_2NR_2^+\ ,$$
$$[Re]COO^- \rightarrow [Re] + CO_2\ .$$

A rhenium-carboxylic acid of the type $CpRe(CO)(N_2Ar)COOH$ has been obtained recently.[45] The authors failed to observe the ν(OH) frequency both in fluorinated oil and in CH_2Cl_2. However, on treatment with NaOD in D_2O the exchange of hydrogen for deuterium was observed—an absorption band at 2240 cm^{-1} appeared in the IR spectrum.

The rhenium complexes $[\eta^5\text{-CpRe(CO)}_2(p\text{-N}_2C_6H_4R)COOH]$, where R = Me, OMe, or NEt_2, have been obtained in the same way, i.e. by treating cationic rhenium complexes with alkali.[45] A band with δ = 8.9 p.p.m., corresponding to the proton in the carboxy-group, has been observed in the ^1H NMR ($CDCl_3$) spectrum. The IR spectrum (CH_2Cl_2) also contains absorption bands at 1954 (v.s.), 1643 (v.s.), and 1596 (v.s.) cm^{-1}. A rhenium hydride complex as well as $[CpRe(CO)_2(N_2Ar)(CO_2^-)]$ are formed in the presence of an excess of alkali as a consequence of the deprotonation of the metal-carboxylic acid. After the irradiation of rhenium carbonyl with UV light in THF in the presence of cyclo-octatetraene, an insignificant amount of a trirhenium-carboxylic acid having the composition $Re_3(CO)_{14}CO_2H$ was detected among the reaction products.[46] The colourless "$Re(CO)_5OH$" complex, which becomes coloured in the light, has been obtained in a quantitative yield by treating the

cationic complex $(CO)_5ReBF_4$ with alkali.[47] Subsequently, this intermediate, which may be a rhenium-carboxylic acid, is converted into a rhenium complex of carbon dioxide. In comparing the results of the synthesis of the rhenium-carboxylic acid obtained by different workers, one must note that the spectroscopic data for the identification of the rhenium-carboxylic acid quoted by Casey et al.[42] agree qualitatively with the spectroscopic data for the rhenium complex of carbon dioxide.[47] It has therefore been suggested[47] that the adduct having the composition "$(CO)_5ReOH$" is the protonated form of the rhenium complex of carbon dioxide formed ultimately: "$(CO)_5$. .ReOH" $\leftrightarrows$ $(CO)_4ReCO_2H$.

There are also literature data concerning the synthesis of stable iron-carboxylic acids.[48] Thus the interaction of aqueous solutions of alkalies with cationic iron complexes made it possible to obtain an iron-carboxylic acid in a pure state:



The compound synthesised is a yellow substance, fairly stable in the presence of atmospheric oxygen, which decomposes on heating above 130 °C. The IR spectrum contains the ν(OCO) = 1565 (m.) and 2700 (m.) cm^{-1} absorption bands. Treatment of the iron-carboxylic acid with potassium hydroxide leads to the formation of the corresponding potassium salt, which can be converted into the iron-carboxylic acid on acidification with hydrochloric acid.

2. Unstable Metal-carboxylic Acids

As can be seen from the foregoing, the problem of the synthesis in one way or another of stable metal-carboxylic acids has been solved in principle, which made it possible to investigate their chemical and physicochemical properties. On the other hand, the hypotheses concerning the existence of unstable metal-carboxylic acids as intermediates had been put forward even earlier. Studies in which the formation of unstable metal-carboxylic acids as intermediates has been claimed can be divided into two groups:

(a) Oxidation of carbon monoxide with water in the presence of transition metal salts. Only hypotheses concerning the formation of metal-carboxylic acids in one of the stages were put forward in these investigations.

(b) The formation of metal-carboxylic acids in the presence of ligands stabilising the metal–carbon σ-bond, such as CO, phosphines, cyclopentadiene (Cp), and others. Under these conditions, it is sometimes possible to obtain an unstable metal-carboxylic acid or at least to achieve the confirmation of its formation by spectroscopic methods.

The existence of metal-carboxylic acids in aqueous solutions was first reported in 1961.[49,50] The authors suggested the formation of a mercury-carboxylic acid as one of the stages in the oxidation of carbon monoxide by water in the presence of mercury salts:[49]

$$Hg^{2+}OH_2 + CO \rightarrow [-Hg-\overset{\overset{O}{\|}}{C}-OH] + H^+ .$$

By analogy with this reaction, the formation of carbon dioxide and hydrogen when carbon monoxide is passed through a solution of univalent thallium hydroxide permitted the conclusion that unstable thallium-carboxylic acid is formed in aqueous solution:[51]

$$TlOH + CO \rightarrow [TlCO_2H] .$$

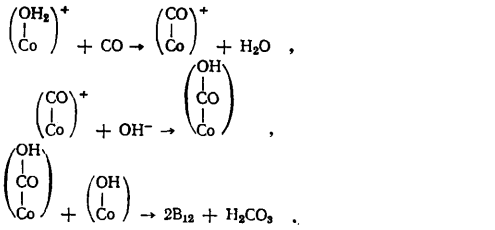
It is also stated in the literature that nickel-carboxylic,[48] silver-carboxylic,[50], and copper-carboxylic[52] acids are formed under analogous conditions. It has been shown in relation to iron-carboxylic acids that the nature of the ligand determines in many respects the stability of these derivatives.[48] The formation of unstable iron-carboxylic acids has also been indicated in other investigations.[53,54] When a cationic platinum complex was treated with water, a platinum hydride complex was obtained as an intermediate.[55] The authors suggest that the reaction proceeds via the formation of a platinum-carboxylic acid:

$$[(Et_3P)_2Pt(Cl)CO]BF_4 \xrightarrow[-HBF_4]{H_2O} [(Et_3P)_2Pt(Cl)CO_2H] \rightarrow [(Et_3P)_2Pt(Cl)H] + CO_2 .$$

The interaction of carbon monoxide with water in the presence of phosphine complexes of zerovalent platinum has been studied in fair detail.[26] The complex $[(iso\text{-}Pr)_3P]_3Pt$ proved to be the most active in this process; a hydroxoplatinum complex is formed on treatment with water in the course of the reaction and interacts further with carbon monoxide, being converted into a platinum-carboxylic acid [ν(OCO) = 1575 cm^{-1}].

There are data on the synthesis of unstable manganese- and rhenium-carboxylic acids on interaction of water with the corresponding metal carbonyl derivatives.[56,57] Derivatives labelled with ^{13}C and ^{18}O were used to identify the intermediates in spectroscopic studies.[57] For example, the interaction of the cationic manganese complex $[dppeMn(CO)_4]^+$ (see Table 1 below) with $H_2{}^{18}O$ results in the formation of the manganese-carboxylic acid $dppeMn(CO)_3.CO^{18}OH$ according to spectroscopic data.

Much attention has been devoted in the literature to the formation of cobalt-carboxylic acids in connection with the modelling of the reactions of vitamin B_{12} by various cobalt chelate complexes.[1,56] Thus the formation of a unstable cobalt-carboxylic acid can be represented schematically in the following way:[58]



The study of processes involving the oxidation of $[Co^I(CN)_2(Et_3P)_2.CO]^-$ by hexacyanoferrate(III) $[Fe(CN)_6]^{3-}$ led to the conclusion that the unstable cobalt-carboxylic acid $[(CN)_5Fe^{II}CNCo^{III}(CN)_2(Et_3P)_2.CO_2H]^{4-}$ is formed in solution.[59]

The formation of unstable rhodium-, iridium- and platinum-carboxylic acids has been postulated in the synthesis by indirect methods of transition metal complexes of carbon dioxide involving treatment of the corresponding hydroxo-complexes of the transition metals with carbon monoxide.[60–63] Thus a familiar carbon dioxide complex has been obtained from the complex $(Ph_3P)_2Rh(CO)OH$:[63]

$$(Ph_3P)_2Rh(CO)OH \xrightarrow{CO+C_6H_6} [(Ph_3P)_2Rh(CO)CO_2H] \rightarrow (Ph_3P)_3Rh_2(CO)_2 \cdot CO_2 \cdot C_6H_6 .$$

The formation of unstable rhodium-carboxylic acids has also been indicated in other communications.[64,65]

An unstable palladium-carboxylic acid is apparently formed on carboxylation of aromatic compounds to the corresponding acids with the aid of palladium acetate in a mixture of glacial acetic acid and its anhydride.[20,21] In this connection, we may note that numerous reactions involving the oxidation of carbon monoxide by water to CO_2 in the presence of palladium salts also probably proceed with formation of a palladium-carboxylic acid.[20]

The synthesis of metal-carboxylic acids from CO_2 and transition metal hydride complexes is a fundamentally new procedure.[1,66] Thus, when a cobalt hydride complex is treated with carbon dioxide, an "anomalous" insertion of a CO_2 molecule in the CO–H bond takes place with formation of an unstable cobalt-carboxylic acid, which was identified by means of chemical reactions.[66]

Table 1. Metal-carboxylic acid esters.

Compound*	Colour	M.p., °C	IR spectrum ν(CO), cm^{-1}	Refs.
$ClHgCO_2Me$	white	109—110	—	[83]
$ClHgCO_2Et$	»	87—88	—	[83]
$MeCO_2HgCO_2Me$	»	109—110	—	[83]
$MeCO_2HgCO_2Et$	»	125	—	[83]
$MeCO_2HgSHgCO_2Me$	»	—	—	[83]
$C_6H_5HgCO_2Me$	»	68—69	—	[84]
p-$MeOC_6H_4HgCO_2Me$	»	89	—	[84]
$Hg(CO_2Me)_2$	»	84	—	[84]
$CpMo(CO)_3CO_2Me$	yellow	47—49	1708	[85]
$(CO)_5MnCO_2Et$	pale-yellow	59,5	1644	[86]
$(Ph_3P)_2Mn(CO)_3CO_2Me$	»	150	1612	[86]
$(Ph_3P)_2Mn(CO_3)CO_2Et$	»	—	1606	[86]
$(Ph_3P)_2Mn(CO)_3CO_2C_5H_{11}$	»	—	1611	[86]
$(Ph_3P)_2MnCO_2CH_2Ph$	»	—	1607	[86]
$CpMn(CO)(NO)CO_2Me$	»	55—57	1650	[87, 88]
$(CO)_5ReCO_2Et$	colourless	69	1635	[89—90]
$(Ph_3P)_2Re(CO)_3CO_2Me$	»	—	1613	[86]
$(CO)_3Re(bipy)CO_2Me$	»	—	1621	[86]
$CpRe(CO)(NO)CO_2Me$	yellow	92—94	1620	[87]
$CpFe(CO)_2CO_2Me$	—	34—36	1665	[85, 88, 91]
$Cp(Ph_3P)Fe(CO)CO_2Me$	yellow	—	1605	[48]
$CpRu(CO)_3CO_2Me$	—	—	—	[92]
$(Ph_3P)_2Ru(CO)_2(I)CO_2Me$	—	—	1651	[92]
$[(C_6H_{11})_3P]Ru(CO)_3CO_2Me$	—	—	1657	[92]
$(Ph_3P)_2Os(CO)_2(Cl)CO_2Me$	—	272—274	1641	[93]
$(Ph_3P)_2Os(CO)_2(Cl)CO_2Et$	—	254—256	1639	[93]
$[(C_6H_{11})_3P]_2Os(CO)_3(Cl)CO_2Me$	—	350	1655	[93]
$[(C_6H_{11})_3P]_2Os(CO)_2(Cl)CO_2Et$	—	—	1652	[93]
$HOs_3C(CO)_{14}CO_2Et$ **	—	—	—	[94]
$IOs_3C(CO)_{14}CO_2Me$ **	—	—	—	[94]
$Ph_3PCo(CO)_3CO_2Et$	yellow	100	1647	[95, 96]
$(PhO)_3PCo(CO)_3CO_2Et$	»	70	1666	[95, 96]
$(Ph_3P)_2Co(CO)_2CO_2Me$	pale-yellow	100	1633	[95, 96]
$(Ph_3P)_2Co(CO)_2CO_2Et$	yellow	90	1627	[95, 96]
$(Salen)_2CoCO_2Me$	—	—	—	[97—99]
$(Salen)_2CoCO_2Me\cdot H_2O$	orange-yellow	—	1716	[97, 98]
$(Salen)_2CoCO_2Et\cdot H_2O$	»		—	[97, 98]
$(Salen)_2CoCO_2Me\cdot Py$ ***	—		—	[97—99]
$RhCl_2(CO)_2CO_2Et$	yellow	—	1705	[100]
$(Ph_3Sb)_3Rh(CO)CO_2Me$	yellow-brown	144	1621	[101]
$(Ph_3P)_2Rh(CO)_2CO_2Me$	yellow	—	1637	[102]
$Rh_4(CO)_{11}CO_2Me$ ****	»	—	1629	[103]
$[Rh_6(CO)_{15}CO_2Et]^-$	—	—	—	[104]
$[(Ph_3P)Rh_6(CO)_{15}CO_2Me]^-$	—	—	—	[104]
$(Me_2PhP)_2IrCl_2(CO)CO_2Me$	white	139—144	1677	[36]
$(Me_2PhP)_2Ir(CO)(Cl_2)CO_2Et$	»	97—100	1663	[36]
$(Me_2PhP)_2IrCl_2(CO)CO_2Ph$	»	167—170	1701	[36]
$(Me_2PhAs)_2IrCl_2(CO)CO_2Me$	»	121—133	1672	[36]
$(Me_2PhAs)_2IrCl_2(CO)CO_2Et$	»	70—72	1664	[36]
$(Me_3P)_2IrCl_2(CO)CO_2Me$	»	159—162	1672	[36]
$(Ph_3P)_2Ir(CO)_2CO_2Me$	»	124—125	1655	[105, 106]
$(Ph_3Sb)_3Ir(CO)CO_2Me$	yellow	156	1612	[101]
$(Ph_3Sb)_3Ir(CO)CO_2Et$	»	148	1608	[101]
$Ir(CO)I_2(bipy)CO_2Me$	»	260	1670	[106]
$Ir(CO)I_2(bipy)CO_2Et$	»	250	1645	[106]
$Ir(CO)I_2(bipy)CO_2Pr\text{-}iso$	»	224	1640	[106]
$Ir(CO)I_2(bipy)CO_2CH_2CH{=}CH_2$	»	178—180	1660	[106]
$Ir(CO)I_2(phen)CO_2Me$	»	300	1654	[106]
$Ir(CO)I_2(Py)CO_2Me$	»	180	1660	[106]
$(Ph_3P)_2Ir(CO)(I_2)CO_2Me$	»	160	1650	[106]
$(Ph_3P)_2Ir(CO)(I_2)CO_2Et$	»	174	1700	[106]
$(Ph_3P)_2Ir(CO)_2(I)CO_2Me$	»	166	1650	[106]
$(Ph_3P)_2Ir(CO)_2(I)CO_2Et$	»	146	1660 1610	[106]
$(Ph_3P)_2Ir(CO)_2(Br)CO_2Et$	»	128—130	1670	[106]
$(Ph_3P)_2Ir(CO)_2(Cl)CO_2Et$	green	110—115	1650	[106]
$(Me_2PhP)_2Ir(CO)Cl_2CO_2Me$	—	—	1677	[106]
$(Me_2PhP)_2Ir(CO)Cl_2CO_2Et$	—	—	1663	[106]
$(Ph_3P)_2\overline{IrCO_2CH_2CH{=}}CH_2(CO)$	colourless	164—166	1662	[107]
$(Ph_3P)_2\overline{IrCO_2CH_2CH{=}}CHMe(CO)_2$	»	146—147	1666	[107]
$(Ph_3P)_2IrCO_2CH_2CH_2OH(CO)_2$	»	135—140	1639	[107]
$(Ph_3P)_2\overline{IrCO_2CH_2CH{=}}CH_2(CO)$	»	160	1660	[108]
$(Ph_3P)_2\overline{IrCO_2CH{\cdot}CH{=}}CHPh(CO)$	»	159	1660	[108]
$(Ph_3P)_2Ir(CO)CO_2Pr\text{-}n$	»	137	1640	[108]
$[(Me_2PhP)_2IrH(CO)(Cl)(HgCl)CO_2Me]^+$	»	165—167	1623	[109]
$[(dmpe)_2Ir(Cl)CO_2Me][FSO_3]$	»		1630	[110]

Table 1 (continued).

Compound*	Colour	M.p., °C	IR spectrum ν(CO), cm^{-1}	Refs.
$[(dmpe)_2IrHCO_2Me][BPh_4]$	»	180	1625	[111]
$[(dmpe)_2Ir(H)CO_2Et][BPh_4]$	»	184	1610	[111]
$[(dmpe)_2Ir(D)CO_2C_2D_5][BPh_4]$	»	182	1598 1610	[111]
$[(Me)_2(CH_2Ph)_2N][Ir_4(CO)_{11}CO_2Me]$	—	—	1645	[112]
$[Ph_4P][Ir_4(CO)_{11}CO_2Me]$	—	—	1650	[112]
Other Ir_4 clusters	—	—	—	[112]
trans-$(Ph_3P)_2Ni(Cl)CO_2Me$	yellow	150—153	1629	[113]
trans-$(Ph_3P)_2Ni(Cl)CO_2Et$	»	134—138	1630	[113]
$(Ph_3P)_2Pd(CO_2Me)_2$	—	118—134	1630	[114]
$(Ph_3P)_2Pd(OCOMe)CO_2Me$	—	129—136	1655	[114]
$(Ph_3P)_2Pd(OCOCF_3)CO_2Me$	—	—	1667	[114]
$(Ph_3P)_2Pd(Cl)CO_2Me$	colourless	190—192	1656, 1672	[21, 80, 113—115]
$(Ph_3P)_2Pd(Cl)CO_2Et$	»	170—190	1633, 1645	[113, 116]
$[(PhO)_3P]_2Pd(Cl)CO_2Et$	»	128—136	1670	[113]
$(t\text{-}C_4H_9NC)_2Pd(Cl)CO_2Me$	»	108—108	1680	[113]
$(t\text{-}C_4H_9NC)_2Pd(Cl)CO_2Et$	»	98—100	1670	[113]
$(t\text{-}C_4H_9NC)_2Pd(Cl)CO_2CH_2Ph$	pale-yellow	137—139	1675	[113]
$(Ph_3P)_2Pd(NCO)CO_2Me$	colourless	225—228	1668, 1653	[117]
$(Ph_3P)_2Pd(NCO)CO_2Et$	»	162—163	1668	[117]
$[(Ph_3P)_2Pd(CO)CO_2Me][BF_4]$	—	—	1668	[117]
$(Ph_3P)_2Pt(CO_2Me)_2$	yellow	178—183	1632	[80, 118]
$(Ph_3P)Pt(OCOCF_3)CO_2Me$	white	188—195	1710, 1692	[119, 120]
$(Ph_3P)_2Pt(OCOCF_3)CO_2Et$	»	185—187	—	[120]
$(Ph_3P)_2Pt(OCOMe)CO_2Me$	»	224—227	—	[120]
$(Ph_3P)_2Pt(Cl)CO_2Me$	»	222—227	1664	[21, 80, 121]
$(Ph_3P)_2Pt(Br)CO_2Me$	»	226—231	1665	[121]
$(Ph_3P)_2Pt(I)CO_2Me$	»	226—229	1655	[121]
$(Ph_3P)_2Pt(Cl)CO_2Et$	»	215—217	1638	[117, 121]
$(Ph_3P)_2Pt(Br)CO_2Et$	»	226—231	1638	[121]
$(Ph_3P)_2Pt(I)CO_2Et$	»	221—229	1638	[121]
$(Ph_3As)_2Pt(Cl)CO_2Me$	»	234—236	1658	[122]
$(Ph_3As)_2Pt(Cl)CO_2Et$	yellow	214—216	1632	[122]
$(Ph_3P)_2Pt(Cl)CO_2Ph$	white	—	1646	[123]
$(Ph_3P)_2Pt(SCN)CO_2Me$	»	230—233	1645	[124]
$(Ph_3P)_2Pt(NO_3)CO_2Me$	»	215—218	1642	[124]
$(Ph_3P)_2Pt(C_6F_5)CO_2Me$	cream	242—245	1660	[124]
$(Ph_3P)_2Pt(C_6H_5)CO_2Me$	white	—	1646	[124]
$(Ph_3P)_2Pt(CH_3)CO_2Me$	»	180—183	1650	[125]
trans-$(Ph_3P)_2Pt(CF_3)CO_2Me$	—	186—188	1655, 1632	[40]
$Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)CO_2Me$	—	190—192	1639	[40]
$Pt(CF_3)(Ph_2PCH{=}CHPPh_2)CO_2Me$	—	206—209	1657, 1643	[40]
$Pt(CH_2CN)(Ph_2PCH{=}{=}CHPPh_2)CO_2CMe_3$		205—208	1638	[40]
$Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)CO_2CHMe_2$		191—193	1633	[40]
$[(Ph_3P)_2Pt(CO)CO_2Me][BF_4]$	white	184—185	1661	[117]
$[(Ph_3P)_2Pt(CO)CO_2Et][BF_4]$	»	149	1660	[117]
$[(Ph_3P)_2Pt(CO)CO_2Me][BF_4]$	»	186—188	1667	[117]
$[(Ph_3P)_2Pt(CO)CO_2Et][BF_4]$	»	182—183	1681	[117]
$(Ph_3P)_2Pt(NCO)CO_2Et$	»	228—230	1656	[117]
$(Ph_3P)_2Pt(Cl)HgCO_2Me_2$	»	185—192	1670	[80]
$(COD)Pt(Cl)CO_2Me$	—	—	1665	[126]
$(Ph_3P)_2Pt(Cl)CO_2CHMe$	—	—	1615	[127]
$(dppe)Pt(OMe)CO_2Me$	—	—	1690	[128]
$(dppe)Pt(CO_2Me)_2$	—	—	1650, 1680	[128, 129]

*Salen = salicylidene-ethylenediamine; bipy = 2,2-bipyridyl; phen = 1,1-phenanthroline; dmpe = dimethylphosphinoethane; dppe = diphenylphosphinoethane; COD = cyclo-octa-1,5-diene; Py = pyridine.

**Characterised by X-ray diffraction.

***The esters of cobalt-carboxylic acids with other *N*-containing ligands have also been obtained.

****Other esters of rhodium-carboxylic acids of the type $[Rh(NO).(Ph_3P)_2(ROH)CO_2R]^+$ as well as rhodium clusters of the type $[Rh_6(CO)_{14}(CO_2Me)_2]^{2-}$ have also been obtained.

Data on the synthesis of a fairly stable chromium-carboxylic acid on radiolysis of tervalent chromium salts in the presence of formic acid in aqueous solutions are also of fundamental importance:[67]

$$[\cdot COOH] + [Cr^{3+}] \rightarrow [CrCO_2H]^{3+},$$

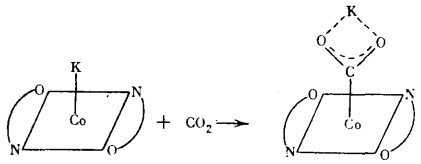
The radical-anion CO_2^- is apparently formed under these conditions and can be stabilised at the metallic centre with subsequent protonation to .COOH. A titanium-carboxylic acid may be formed under analogous conditions.[1] These results are important for the

understanding of the mechanism of the reduction of carbon dioxide to organic compounds in aqueous solutions in the presence of transition metal compounds.

III. METAL-CARBOXYLIC ACID SALTS AND POLYNUCLEAR TRANSITION METAL COMPLEXES OF CARBON DIOXIDE

As already mentioned above, treatment of a platinum-carboxylic acid with potassium hydroxide can yield an equivalent amount of the potassium salt of the platinum-carboxylic acid,[26] which has been characterised by IR and NMR spectroscopic methods.

There have been reports of attempts to obtain salts of metal-carboxylic acids by inserting carbon dioxide in the transition metal–alkali metal (or alkaline earth metal) bond. Thus treatment of the organometallic analogue of a Grignard reagent $C_6H_5(Ph_3P)NiMgBr$ with CO_2 results in the formation of the unstable $Cp(Ph_3P)NiCO_2.MgBr$, the complex $Cp_2Ni(CO)_2$ being formed as the final product on hydrolysis.[68] When carbon dioxide was passed through a solution of the potassium salts of complexes of the type $K(Co)(Salen)_2$ (where Salen = silicylidene-ethylenediamine), the insertion of a CO_2 molecule in the cobalt–potassium bond was observed:[69,70]



When sodium salts of manganese and rhenium hydride carbonyls are treated with carbon dioxide, a CO_2 molecule is also inserted in the transition metal–sodium bond.[71] The product of the interaction of carbon dioxide with the sodium salt of the rhenium compound was then characterised spectroscopically and with the aid of chemical reactions as the sodium salt of a rhenium-carboxylic acid. However, in the light of latest data concerning the synthesis of trirhenium-carboxylic acids,[46,47] further studies on these lines are essential in order to elucidate the question whether or not the compound obtained by Lysak et al.[71] is a rhenium cluster with CO_2.

It has been shown recently that carbon dioxide can be inserted also in the iron–magnesium bond:[72]

$$[(\eta\text{-CpFe(CO)}_2]_2Mg + CO_2 \rightarrow [(\eta\text{-Cp})(CO)_2FeCO_2]_2Mg\,.$$

Alkylation of this salt with methyl iodide yielded the methyl ester of the iron-carboxylic acid.

When aluminium halides interact with the iridium-carboxylic acid ester $(Ph_3P)_2Ir(CO)_2CO_2Me$ in the presence of traces of moisture, a complex of carbon dioxide coordinated simultaneously to iridium and aluminium atoms is formed.[73,74] It has been shown that carbon dioxide is displaced from this compound by triphenylphosphine and carbon monoxide and that, following the replacement of $^{12}CO_2$ by $^{13}CO_2$, the 1725, 1375, and 1220 cm^{-1} bands are displaced to 1700, 1340, and 1210 cm^{-1} respectively.

Overall, the study of reactions in which compounds of CO_2 coordinated to a transition metal atom and to alkali or alkaline earth metals are formed is important for the solution of problems associated with the introduction of CO_2 molecules into catalytic processes (bifunctional catalysis).[75–77]

Considerable difficulties arise in the interpretation of experimental data concerning the nature of these products. It has been shown by X-ray diffraction that the product of the insertion of the CO_2 molecule in the cobalt–potassium bond is in reality not a salt of a cobalt-carboxylic acid but a complex of carbon dioxide.[70] On the other hand, the insertion of a CO_2 molecule in the rhenium–sodium bond is irreversible. Depending on the nature of the metal and the ligand, one can probably expect the formation of metal-carboxylic acid salts in some cases and of transition metal complexes of carbon dioxide in others.

One can assume that the formation of metal-carboxylic acids on interaction of hydroxo-complexes with carbon dioxide can lead to the formation of transition metal complexes of carbon dioxide, for example via the mechanism

$$[M]OH + [M']CO_2H \rightarrow [M']CO_2[M] + H_2O$$

In this case the dinuclear (polynuclear) complexes formed can be regarded as derivatives (salts) of the corresponding metal-carboxylic acids. Indeed, it has been found that the interaction of carbon monoxide with the hydroxorhodium complex $(Ph_3P)_2Rh(CO)OH$ leads to the formation of a rhodium complex of carbon dioxide: $(Ph_3P)_3Rh_2(CO)_2CO_2C_6H_6$.[63] Analogous reactions occur also when hydroxo-complexes of transition metals, namely $[Me_3PtOH]_4$, $(Ph_3P)_2Ir(CO)OH$, etc., are treated with carbon monoxide.[60–62] The formation of the rhenium complex of carbon dioxide $(CO)_5ReCO_2.[Re(CO)_4]_2$ also probably proceeds via the formation of an unstable rhenium-carboxylic acid.[47] The IR spectrum of the resulting compound contains absorption bands characteristic of transition metal complexes of CO_2 [1458 (s.), 1165 (br.), and 1150 (s.) cm^{-1}]. According to X-ray diffraction data, the CO_2 molecule is coordinated to three metal atoms. We may note that the IR spectra of metal-carboxylic acids usually contain one ν(CO) absorption band, while in the case of carbon dioxide complexes the spectra show three absorption bands.[1,2] The data of Casey et al.,[42] demonstrating that the IR spectrum (nujol) of the rhenium-carboxylic acid $CpRe(CO)(NO)CO_2H$ which they obtained contains three intense absorption bands near 1585 (s.), 1145 (s.), and 1135 (s.) cm^{-1}, correspond better to a rhenium complex of carbon dioxide, although they observed also absorption bands corresponding to the vibrations of the hydroxy-group near 2960 (w.), 2860 (w.), 2705 (w.), and 2690 (w.) cm^{-1}.

The ruthenium and osmium complexes of carbon dioxide are probably formed on treatment of the corresponding metal carbonyls with alkalies also via the intermediate formation of metal-carboxylic acids.[78,79] According to X-ray diffraction data, the CO_2 molecule in the osmium complex $[HOs_3(CO)_{10}CO_2Os_6(CO)_{17}]^-$ is linked to three metal atoms.[79]

IV. ESTERS OF METAL-CARBOXYLIC ACIDS (ALKOXY-CARBONYL COMPLEXES OF TRANSITION METALS)

1. Synthesis

The most widely used and convenient methods from the preparative point of view are as follows:[8]

(1) Treatment of the carbonyl group coordinated to the metal with solutions of alkalies in alcohol:

$$[M]CO + OR^- \rightarrow \{[M]CO_2R\}^-\,,$$

Treatment of cationic complexes of metal carbonyl derivatives with alcohols is a modification of this method.

(2) Treatment of halogeno-derivatives of transition metal complexes with alcoholic alkalies in the presence of carbon monoxide, for example:

$$(Ph_3P)_2PtCl_2 + CO + NaOH/ROH \rightarrow (Ph_3P)_2Pt(CO_2R)_2\,,$$

Treatment of alkoxo-complexes of transition metals directly with carbon monoxide leads to the same results.

(3) Exchange reactions between chloroformic acid esters and transition metal hydride salts, for example:

$$NaMn(CO)_5 + ClCO_2CH_3 \rightarrow (CO)_5MnCO_2CH_3 .$$

(4) Reactions involving the oxidative addition of chloroformic acid esters to transition metal complexes, for example:

$$(Ph_3P)_3Pt + ClCO_2R \rightarrow (Ph_3P)_2Pt(Cl)CO_2R .$$

(5) Treatment of transition metal isocyanate complexes with carbon monoxide and alcohol:

$$(Ph_3P)_2Pd(NCO)_2 \xrightarrow{ROH;CO} (Ph_3P)_2Pd(CO_2R)_2 ,$$

(6) Alkylation of metal-carboxylic acid salts:[72]

$$[(\eta\text{-Cp})Fe(CO)_2CO_2]_2Mg + CH_3I \rightarrow (\eta\text{-Cp})Fe(CO)_2CO_2CH_3 .$$

(7) Transfer of the CO_2R group from an organomercury derivative to a transition metal complex via the oxidative addition mechanism:[80,81]

$$(Ph_3P)_4Pd + ClHgCO_2R \rightarrow (Ph_3P)_2Pd(Cl)CO_2R + Hg .$$

(8) Direct action of carbon dioxide on transition metal complexes containing a metal–carbon σ-bond:[82]

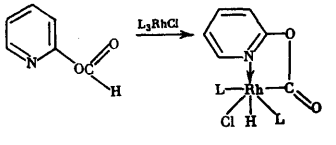
$$M^{\delta-}—R^{\delta+} + CO_2 \rightarrow MCO_2R .$$

(9) Esters of metal-carboxylic acids can be obtained also by esterifying the carbamoyl complexes of transition metals. Table 1 lists the metal-carboxylic acid esters described in the literature.

Esters of metal-carboxylic acids are also formed on decomposition of keto-acids in solution or on their thermolysis:[130]

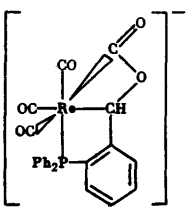
$$(Ph_3P)_2Pd(Cl)COCO_2R \rightarrow (Ph_3P)_2Pd(Cl)CO_2R + CO .$$

Yet another method of synthesis of metal-carboxylic acid esters is *ortho*-metallation. Thus the interaction of α-pyridyl formate with the complex $[Rh(Ph_3P)_3Cl]$ can yield the ester of a rhodium-carboxylic acid:



The disproportionation of CpRe(CO)(NO)CHO results in the formation of the complex $Cp(CO)(NO)ReCO_2CH_2Re(CO)(NO)Cp$, which can be regarded as a rhenium-carboxylic acid ester.[132] Treatment of the ester with methanol results in the formation of CpRe.(CO)(NO)CO_2Me (m.p. 105–115 °C; IR spectrum: 1626 and 1010 cm^{-1} in nujol).

A rhenium-carboxylic acid ester has been obtained to which the following structure was attributed on the basis of IR and ^1H NMR spectroscopic data:[133]



After alkylating an iridium complex of carbon dioxide with $MeSO_3F$, the methyl ester of an iridium-carboxylic acid was isolated:[110]

$$(dmpe)_2Ir(Cl)CO_2 + MeSO_3F \rightarrow [(dmpe)_2Ir(Cl)CO_2Me][SO_3F],$$

dmpe = dimethylphosphinoethane

The IR spectrum contains absorption bands at 1630 and 1065 cm^{-1}.

2. Investigation by Physicochemical Methods

As can be seen from Table 1, the IR spectroscopic method yields an extremely large amount of information in the study of metal-carboxylic acid esters. The MCA esters have characteristic absorption bands, as a rule with appreciable intensity, corresponding to the ν(OCO) frequencies of the ester group in the range 1600–1700 cm^{-1} and the ν(OR) frequencies in the range 1000–1070 cm^{-1}. A fairly large number of metal-carboxylic acid esters, which cannot be isolated as pure compounds from the reaction mixture, were characterised by this method.

There exist also data obtained by investigating metal-carboxylic acid esters in solutions by UV spectroscopy. Thus studies have been made of the UV spectra of complexes of the type $(Ph_3P)_2Pt(Cl)CO_2.CH_2R$, where R = H, Me, or Ph.[123] The following values of 10^{-4} ε (λ_{max}, nm) were found for R = H: 2.3 (257); 1.6 (268); 1.1 (275). The corresponding values for the ethyl and benzyl esters are close to those for the methyl ester.

The ^1H NMR method is used widely for the identification of metal-carboxylic esters. Data obtained by determining the dipole moments permitted the conclusion that platinum-dicarboxylic acid esters of the type $(Ph_3P)_2Pt(CO_2Me)_2$ have the *trans*-structure.[118]

It is noteworthy that metal-carboxylic acid esters are the *C*-isomers of the corresponding carboxylate complexes of transition metals (*O*-isomers),[134] for example: $Hg(CO_2R)_2$ and $Hg(OCOR)_2$; $(CO)_5ReCO_2R$ and $(CO)_5ReOCOR$; $(Ph_3P)_2Pt(CO_2R)_2$ and $(Ph_3P)_2.Pt(OCOR)_2$; $(Ph_3P)_2Pd(CO_2R)_2$ and $(Ph_3P)_2Pd(OCOR)_2$. The method of X-ray electron spectroscopy has been applied successfully in the solution of the problem of the mode of coordination of carbon dioxide in the complex $(Ph_3P)_2PtCO_2$.[135]

Table 2 lists the bond lengths in metal-carboxylic acid esters determined by X-ray diffraction.

Table 2. X-Ray diffraction data for metal-carboxylic acid esters.

Compound	Bond length, Å			O–C–O angle, deg	Refs.
	M–C	C=O	C–O		
$ClHgCO_2Me$	1.96	1.24	1.26	114	[136]
trans-$(Ph_3P)_2Pt(CO_2Et)_2$	2.059 (7)	1.228 (7)	1.351 (7)	119.5 (6)	[137]
$[(dmpe)_2Ir(Cl)CO_2Me][FSO_3]$	2.073 (8)	1.151 (10)	1.366 (10)	123.0 (8)	[110]
(bipy)$Ir(I_2)(CO)CO_2Me$	2.05 (2)	1.18 (2)	1.28 (2)	120.6	[138]
$[NMe_3(CH_2Ph)_2][Ir_4(CO)_{11}CO_2Me]$	2.20 (4)	1.13 (6)	1.27 (6)	—	[112]
$HOs_3C(CO)_{14}CO_2Et$	2.028 (15)	1.28 (2)	1.34 (3)	—	[94]
$IOs_3C(CO)_{14}CO_2Me$	2.02 (4)	1.28 (5)	1.29 (5)	—	[94]
$[Rh_6(CO)_{15}CO_2Me]^-$	1.96 (2)	1.18 (3)	1.31 (3)	109.2	[139]

3. Reactions

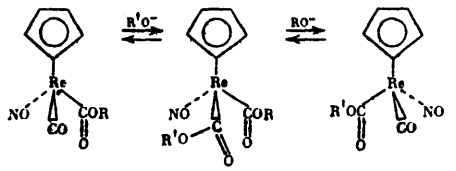
(a) Transesterification. One of the widely investigated reactions of metal-carboxylic acid esters is transesterification:

$$[M]CO_2R + R'OH \rightleftarrows [M]CO_2R' + ROH .$$

It has been shown for an iron-carboxylic acid ester that the ease of this reaction is due to the existence in solution of the equilibrium:[42]

$$Cp(Ph_3P)Fe(CO)CO_2Me \rightleftarrows Cp(Ph_3P)Fe(CO)_2^+ + OMe^- .$$

The existence of such equilibrium has been confirmed by IR and ^1H NMR spectroscopic methods. The compound $CpFe(CO)(Ph_3P).CO_2Me$ [ν(OCO) = 1630 cm^{-1}] has been obtained in an optically inactive form by the transesterification of the (-)$CpFe(CO)(Ph_3P).CO_2C_{10}H_{19}$ [ν(OCO) = 1615 cm^{-1}] diastereoisomers with methyl alcohol.[140] The following mechanism has been proposed for the transesterification of rhenium-carboxylic acid esters:[132]



The interaction of the allyl alcohols $H_2C=C(R)CH_2OH$ with the methyl ester of an iridium-carboxylic acid leads to the formation of cyclic esters of the type $(Ph_3P)_2COIrCO_2CH_2C(R)=CH_2$ as a result of transesterification (Table 1).

Metal-carboxylic acid esters are formed readily also when carbamoyl complexes of transition metals are treated with alcohols, which can also be regarded as a method of their synthesis. On the other hand, when metal-carboxylic acid esters are treated with amines, the reverse reaction is observed, i.e. metal-carboxylic acid esters are formed.[141,142]

(b) Reactions with alkyl halides. When metal-carboxylic acid esters interact with alkyl halides, the corresponding new esters are formed:[82]

$$[M]CO_2R + R'X \rightarrow R'CO_2R + [M]X .$$

(c) Interaction with acids. In acid hydrolysis of the esters, one observes as a rule the decomposition of the metal-carboxylic ester to the corresponding alcohol and carbon monoxide. As mentioned above, an iridium-carboxylic acid may be obtained by treating the iridium-carboxylic acid $(Me_2PhP)_2Ir(CO)Cl_2(CO_2Me)$ with hydrogen chloride.[36]

The reactions of cationic complexes with the various reagents, leading to the formation of metal-carboxylic acid esters, have been briefly characterised.[117]

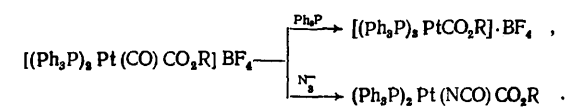
(d) Hydrolysis. When metal-carboxylic acid esters interact with water, carbon dioxide is evolved and a hydride complex is formed. This reaction probably proceeds via the intermediate formation of a metal-carboxylic acid:[143]

$$(Ph_3P)_2Pt(Cl)CO_2R + H_2O \rightarrow [(Ph_3P)_2Pt(Cl)CO_2H] \rightarrow (Ph_3P)_2Pt(H)Cl + CO_2 .$$

(e) Thermal decomposition. Carbon dioxide is evolved in the thermolysis of the methyl ester of an iridium-carboxylic acid and an iridium hydride complex is formed:[36]

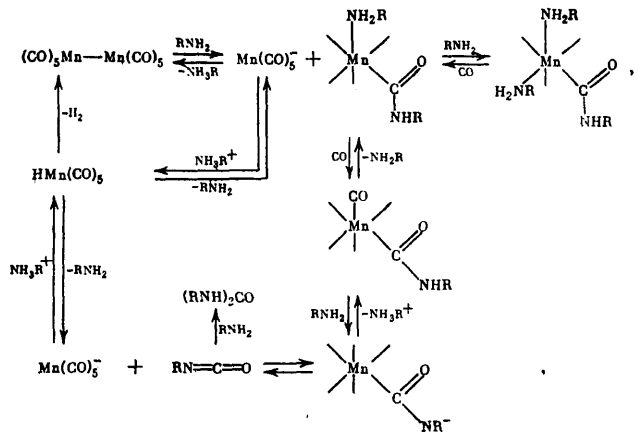
$$(Me_2PhP)_2Ir(CO)Cl_2(CO_2Me) \rightarrow (Me_2PhP)_2Ir(CO)(H)Cl_2 + CO_2 .$$

(f) Other reactions. Among other reactions, the interaction of cationic complexes containing the CO_2R group various reagents, leading to the substitution or modification of the ligand, is of some interest:[117]



V. AMIDES OF METAL-CARBOXYLIC ACID (CARBAMOYL COMPLEXES OF TRANSITION METALS)

As already mentioned above, the formation of MCA amides as intermediates is observed in the reactions involving the carbonylation of amines by carbon monoxide in the presence of catalysts. According to Dombek and Angelici,[144] the mechanism of this reaction can be represented schematically in the following manner:



The study of the carbonylation of amines in the presence of iron[145,146] and manganese[144] carbonyls led to the conclusion that the corresponding carbamoyl derivatives are formed in the course of the process, for example, *cis*-$Mn(CO)_4(NH_2R)CONHR$ on carbonylation of n-butylamine.[144] A series of amides of a nickel-carboxylic acid (carbamoyl derivatives) having the general formula $(PNP)Ni(Cl).CONHR$, where PNP is the ligand and R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, n-Bu, etc., have been obtained in a study of the carbonylation of amines with carbon monoxide in the presence of nickel chloride and 2,6-bis(diphenylphosphinomethyl)pyridine (PNP) as the ligand.[147]

The alkoxycarbonylation reactions of the amines probably proceed via the intermediate formation of carbamoyl complexes.[148,149]

1. Methods of Synthesis of Metal-carboxylic Acid Amides

The general methods of synthesis of MCA amides (carbamoyl complexes of transition metals) have been described.[8,142] Among the methods of preparation of carbamoyl derivatives, the following may be noted:

(1) Exchange reactions of the type

$$(CO)_nMnNa + ClCONR_2 \rightarrow (CO)_nMnCONR_2 + NaCl .$$

(2) Oxidative addition reactions:

$$(Ph_3P)_3Pd + ClCONR_2 \rightarrow (Ph_3P)_2Pd(Cl)CONR_2 + Ph_3P .$$

(3) Syntheses via mercury-carboxylic acid amides[80] of the oxidative addition type.

(4) Interaction of metal carbonyls or their derivatives with primary and secondary amines:

$$Mn(CO)_5+RNH_2\rightarrow Mn(CO)_4(CONHR)(RNH_2) \text{ etc.}$$

In terms of their reactivity, metal carbonyls can be divided into three groups.[8] It was found that the reactivity can be related to the M–CO bond force constant, which can be obtained from spectroscopic data. Such correlation permits the prediction of the course of these reactions via one pathway or another: the formation of stable carbamoyl complexes, the establishment of equilibrium, and, finally, the absence of any interaction.

(5) Interaction of cationic complexes of transition metals with NaNRR′, isocyanates or quaternary ammonium salts.[142]

(6) Aminolysis of metal-carboxylic acid esters. The rate of this reaction diminishes with increase in the size of the group at the nitrogen atom:[142] $MeNH_2 \gg EtNH_2 \gg Me_2NH > Me(CH_2)_3NH_2 > Me_2CHNH_2 \geqslant Me_3CNH_2$.

(7) Insertion of alkyl isocyanates in a metal–hydrogen bond, for example:

$$CpFe(CO)_2H+MeNCO\rightarrow CpFe(CO)_2CONHMe \ .$$

(8) Interaction of isonitrile complexes of transition metals with alkalies:[150]

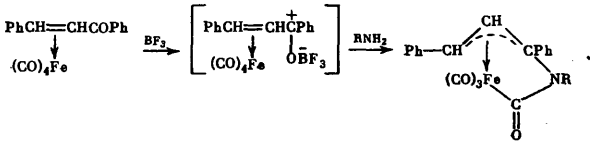
$$(Ph_3P)_3Pt(CNMe)_2^{2+}+OH^-\rightarrow(Ph_3P)_2Pt(CNMe)CONHMe^+ \ .$$

(9) Insertion of carbon monoxide in the $M-NR_2$ bond. This reaction proceeds under mild conditions in the case of coordination compounds of the actinides:[151]

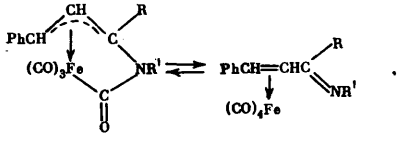
$$M(\eta\text{-}C_5Me_5)_2NR_2(Cl)+CO\rightarrow M(\eta\text{-}C_5Me_5)_2(\eta^2\text{-}CONR_2)Cl \ .$$

The reaction is extremely important as one of the stages in the carbonylation of amines by carbon monoxide in the presence of catalysts.

Stable carbamoyl complexes of iron are formed from the adduct of (*C*-chalcone)$Fe(CO)_4$ with boron trifluoride, its formation being followed by treatment with primary amines:[152–154]



The carbamoyl derivatives with the R = Me and C_6H_{11} groups obtained in this way consist of yellow crystals which are extremely stable in air and have distinct melting points. The equilibrium



has been investigated by IR spectroscopy.[154] It was shown that, when the group R is large, the equilibrium is displaced to the left, while in the case where the group R′ at the nitrogen atom is large the equilibrium is displaced to the right.

Anionic complexes constitute a special type of compound incorporating the carbamoyl group. Thus the interaction of tetrakis(dimethylamino)methane with iron or nickel carbonyl [155] results in the formation of stable carbamoyl complexes:

$$M(CO)_n+C(NMe_2)_4\rightarrow[C(NMe_2)_3][(CO)_{n-1}MCONMe_2]\xrightarrow{R_2NH}[C(NMe_2)_3][(CO)_{n-1}MCONR_2]$$

M=Fe, Ni

When an anionic iron complex containing the carbamoyl group is treated with a nickel salt, a complex is formed in which the carbamoyl group plays the role of the bridging ligand (η^2-coordination):[156]

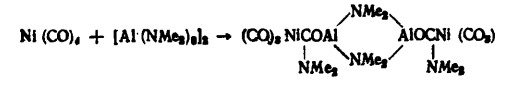
$$[C(NMe_2)_4][(CO)_4FeCONR_2]+NiBr_2\rightarrow[(CO)_4FeCONR_2]_2Ni \ .$$

R=Me_2, $(CH_2)_4$, $(CH_2)_5$

The interaction of nickel carbonyl with lithium dimethylamide leads to the formation of a carbamoyl complex of nickel:[157]

$$Ni(CO)_4+LiNMe_2\rightarrow Li[(CO)_3NiCONMe_2] \ .$$

An analogous reaction takes place also between nickel carbonyl and $[Al(NMe_2)_3]_2$ [158] or $Ti(NMe_2)_4$:[159]



The results obtained in the syntheses of stable metal-carboxylic acid amides are summarised in Table 3.

Table 3. Stable metal-carboxylic acid amides.

Compound	Colour	M.p., °C	ν(CO), cm^{-1}	Refs.
$ClHgCONEt_2$	white	66–68	1575	[80]
$Hg(CONMe_2)_2$	»	148–149	1555	[33]
$Hg(CONEt_2)_2$	»	138–139	1575	[33]
$Hg(CONMeCH_2Ph)_2$	»	138	1560	[33]
$Hg(CON(CH_2)_4]_2$	»	96	1530	[33]
$Hg[CON(CH_2)_5]_2$	»	102	1555	[33]
$Hg[CON(CH_2)_4O]_2$	»	196	1560	[33]
$CpMo(CO)_3CONMe_2$	—	—	1594	[160]
$CpMo(CO)_3CONHMe$	—	—	1614	[160]
$CpMo(CO)_3CON(CH_2)_5$	orange-yellow	70	1590	[160]
$CpW(CO)_3CONHMe$	yellow	122–124	1597	[160]
$CpW(CO)_3CONHCMe_3$	orange	—	1627	[160]
$CpW(CO)_3CONMe_2$	yellow	117–119	1576	[160]
$CpW(CO)_3CON(CH_2)_5$	orange-yellow	110	1571	[160]
η^5-$CpW(CO)_3(MeNH_2)CONHMe$	orange	100–115	1600	[161]
η^5-$CpW(CO)_3(Ph_3P)CONHMe$	yellow	186	1550	[161]
η^5-$CpW(CO)_3(MeCN)CONHMe$	brown	164	1575	[161]
$Mn(CO)_4(NH_2)CONH_2$	—	—	1518, 1501	[162]
$Mn(CO)_3(Ph_3P)(NH_2)CONH_2$	pale-yellow	140	1520, 1508	[162]
$Mn(CO)_4(MeNH_2)CONHMe$	—	75	1605	[163]
$Mn(CO)_4(EtNH_2)CONHEt$	—	105	—	[163]
$Mn(CO)_4CON(p\text{-}MeOC_6H_4)CHN(p\text{-}MeOC_6H_4)$	—	111–112	1693	[164]
$Mn(CO)_4CON(p\text{-}Me_6H_4)CHN(p\text{-}MeC_6H_4)$	—	119–120	1697	[164]
$Mn(CO)_4CONPh(CHNPh)$	—	118–119	1699	[164]
$Mn(CO)_4CON(p\text{-}ClC_6H_4)CHN(p\text{-}ClC_6H_4)$	—	122–125	1703	[164]
$Mn(CO)_4CON(p\text{-}FC_6H_4)CHN(p\text{-}FC_6H_4)$	—	115–116	1704	[164]
$Mn(CO)_4(Ph_3P)CONH_2$	pale-yellow	—	1605, 1580, 1553	[165]
$Mn(CO)_3(Ph_3P)_2CONH_2$	»	—	—	[165]
$Mn(CO)_3(Et_3P)_2CONH_2$	»	—	1600, 1572	[165]
$Mn(CO)_3(bipy)CONH_2$	orange-red	—	1598, 1543	[165]
$Mn(CO)_3(phen)CONH_2$	»	—	1602, 1580, 1550	[165]
$Mn(CO)_3(Ph_3P)_2CONHMe$	yellow	—	—	[166]
η^5-$CpMn(CO)(NO)CONH_2$*	—	—	—	[167]
$Me_4C_4Mn(CO)_2CONH_2$	yellow	—	1546	[168]
$Me_4C_4Mn(CO)_2CONC_6H_{11}$	»	—	1589	[168]
$Re(CO)_4(MeNH_2)CONHMe$	colourless	—	1610, 1511, 1486	[169]
$Re(CO)_4(NH_2)(CONH_2)$	»	—	1640, 1618, 1497	[169]
cis-$Re(CO)_4(Me_2CHNH_2)CONHCHMe_2$	—	—	—	[170]
$Re(CO_4)CON(p\text{-}MeOC_6H_4)CHN(p\text{-}MeOC_6H_4)$	—	115–117	1696	[164]

Table 3 (continued).

Compound	Colour	M.p., °C	ν(CO), cm^{-1}	Refs.
$Re(CO)_4CON(p\text{-}MeC_6H_4)CHN(p\text{-}MeC_6H_4)$	—	119—121	1703	[164]
$Re(CO)_4CONPh(CHNPh)$	—	114—116	1708	[164]
$Re(CO)_4CON(p\text{-}ClC_6H_4)CHN(p\text{-}ClC_6H_4)$	—	180—182	1711	[164]
$Re(CO)_4CON(p\text{-}FC_6H_4)CHN(p\text{-}FC_6H_4)$	—	125—127	1709	[164]
$CpFe(CO)_2CONH_2$	—	—	1593	[92]
$CpFe(CO)_2CONHC_6H_{11}$	yellow	116—117	1635	[171]
$CpFe(CO)_2CONHMe$	—	118	1625	[91]
$CpFe(CO)_2CONHEt$	—	97	1622	[91]
$CpFe(CO)_2CONHCHMe_2$	—	78—80	1620	[91]
$CpFe(CO)_2CON(CH_2)_5$	—	70	1580	[91]
$CpFe(CO)(Ph_2P)CONHMe$	—	114	1558	[91]
$CpFe(CO)_2CONMe_2$	—	111—112	1545, 1530	[172]
$CpFe(CO)_2CONEt_2$	—	75—76,5	1534	[172]
$CpFe(CO)_2CONHCMe_3$	yellow	95—97	1633	[173]
$CpFe(CO)(CNCMe_3)CONHCMe_3$	pale-yellow	—	1609	[173]
$Fe(CO)_2(Ph_3P)_2(Br)CONH_2$	—	—	1565, 1558, 1532	[174]
$Ru(CO)_2(Ph_3P)_2(Cl)CONH_2$	—	—	1575, 1568, 1545	[174]
$CpRu(CO)(Et_3P)CONH_2$	—	—	—	[175]
$CpRu(CO)(Ph_3P)CONH_2$	—	—	—	[175]
$CpRu(CO)(CNMe)CONH_2$	—	—	—	[175]
$CpRu(CO)_2CONH_2$	—	—	—	[175]
$CpRu(CO)_4CONHMe$	—	—	1631	[92]
$CpRu(CO)_2CONHC_6H_{11}$	—	—	1621	[92]
$CpRu(CO)_2CONHBu\text{-}n$	—	—	1626	[92]
$CpRu(CO)_2CONHCHMe_2$	—	—	1628	[92]
$Os(CO)_3(Ph_3P)_2(Cl)CONH_2$	—	—	1575, 1530	[174]
$Os(CO)_3[P(C_6H_{11})_3]_2(Cl)CONH_2$	—	—	1567, 1529	[174]
$Co(CO)_3(Ph_3P)CON(CH_2)_5$	yellow	—	1591	[176]
$Co(CO)_3(Ph_3P)CON(Pr\text{-}n)_2$	»	—	1598	[176]
$Rh_6(CO)_{16}CONH(CHMe_2)$	—	—	1630	[104]
$(Ph_3P)_2Pd(Cl)CONHMe$	white	—	1628	[177]
$(Ph_3P)_2Pd(Cl)CONMe_2$	»	—	1598	[177]
$(Ph_3P)_2Pd(Cl)CONMeEt$	»	—		[177]
$(MePh_2P)_2Pd(Cl)CONMe_2$	yellow-orange	—		[177]
$(Ph_3P)_2Pd(Cl)CONEt_2$	white	164	1590	[80]
$(Ph_3P)_2Pt(Cl)CONMe_2$	»	—	1586	[177]
$(Ph_3P)_2Pt(I)CONMe_2$	pale-orange	—	1570	[177]
$(Ph_3As)_2Pt(Cl)CONMe_2$	white	—	1585	[177]
$(MePh_2P)_2Pt(Cl)CONMe_2$	»	—	1565	[177]
$(Me_2PhP)_2Pt(Cl)CONMe_2$	»	—		[177]
$(Ph_3P)_2Pt(Cl)CONMeEt$	»	—		[177]
$(Ph_3P)_2Pt(Cl)CONHMe$	»	—	1600	[177]
$(Ph_3P)_2Pt(Cl)CONHEt$	»	—	1601	[177]
$(Ph_3P)_2Pt(Cl)CONEt_2$	»	237	1580	[80, 177]
$(Ph_3As)_2Pt(Cl)CONEt_2$	»			[177]
$(Ph_3As)_2Pt(Cl)CONHCHMe_2$	»	—	1616	[177]
$(Ph_3P)_2Pt(NCO)CONMe_2$	—	—	1580	[177]
$(Ph_3P)_2Pt(CONEt_2)_2$	—	134	—	[80]
$(Ph_3P)_2Pt(CONEt_2)HgCONEt_2$	—	70	1690, 1650	[80]
$[NH_2(CHMe_2)_2]\ [cis\text{-}Pt(CO)Cl_2CON(CHMe_2)_2]$	—	—	—	[178]
$[(Ph_3P)_2Pt(NCMe)CONHMe][BF_4]$	pale-yellow	183—185	—	[179]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONMe_2)Cl$	—	—	1546	[151]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONEt_2)Cl$	—	—	1516	[151]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONMe_2)NMe_2$	—	—	1521	[151]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONMe_2)_2$	—	—	1523	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONMe_2)Cl$	—	—	1559	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONEt_2)Cl$	—	—	1537	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONMe_2)NMe_2$	—	—	1521	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONMe_2)_2$	—	—	1529	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONEt_2)_2$	—	—	1499	[151]

*Characterised by X-ray diffraction analysis.

2. Investigation of Metal-Carboxylic Acid Amides by Physicochemical Methods

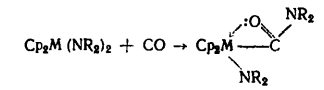
One of the principal physicochemical methods used to study MCA amides is IR spectroscopy. With the aid of this method, it is possible to identify in most cases the CO and NH groups, although in many instances the identification of the vibration frequencies of the carbonyl group may be difficult owing to the superposition of the broad band due to the deformation vibrations of the NH group.[8] The bands of the carbonyl group are observed over a fairly wide range and are sensitive to the solvent employed in the measurement.[163]

The ^{1}H NMR methods yields much information for the identification of substituents at the nitrogen atom (see, for example, Refs.147, 165, and 179). This method has been used successfully also in the study of the reactions involving the transformation of the carbamoyl group into the amidine group.[163] The signal of the carbon atom of the carbamoyl group can also be identified by NMR. In the case of cobalt-carboxylic acid amides it is located within a fairly wide range of values of δ (183—213 p.p.m).[180]

The mass-spectrometric method has also been used to identify metal-carboxylic amides (see, for example, Angelici and Blacik[168]).

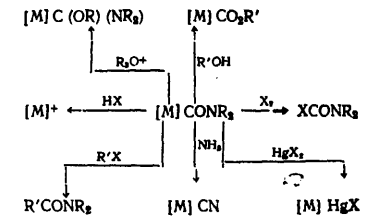
A study in which the structure of the complex $Mn(CO)_4(MeNH_2)$. .CONHMe had been established by X-ray diffraction[8] was for a long time the only structural study available. However, recently X-ray diffraction data have been published on the coordination of the carbamoyl group with other metals. It has been established that the carbamoyl group can function both as a monodentate ligand, for example, in *trans*-$(Et_3P_2)Ni(I)CONEt_2$,[181] and a bidentate ligand. In the latter case, the carbon and oxygen atoms of the carbamoyl group can be linked to a single metal atom, for example, in $(\eta\text{-}C_5Me_5)_2Th$. .$(\eta^2\text{-}CONEt_2)Cl$ [151] or can function as a bridge between two metal atoms as in $HRu_3(CO)_{10}CONMe_2$.[182] It has been noted[151] that on η^2-coordination the C—O bond is lengthened compared with the usual coordination of this group to a metal. The pronounced shortening of the metal—oxygen bond in the uranium complex compared with the uranium—carbon bond was attributed by the authors to the high affinity of uranium for oxygen. Table 4 presents data obtained in X-ray diffraction studies on the carbamoyl complexes.

Clearly the results of X-ray diffraction analysis have posed a number of problems in this field which can be solved with the aid of IR and NMR spectroscopic methods. Indeed, data concerning the mode of coordination of the carbamoyl group can be obtained with the aid of IR spectra. Furthermore, it is apparently possible to estimate by NMR the contribution of a particular structure in the reaction, as shown by Fagan et al.:[151]



3. Reactions of Metal-Carboxylic Acid Amides (Carbamoyl Derivatives)

The chemical reactions of carbamoyl complexes of transition metals have been considered in a review:[8]



The thermal stability of the isostructural iron, ruthenium, and osmium carbamoyls has been investigated.[184] The authors showed that the stability of these compounds increases in the sequence Fe < Ru < Os. A study,[185] in which the interaction of a cationic manganese complex with amines, namely

$$Mn(CO)_4(MeCN)_2^+ + MeNH_2 \rightarrow Mn(CO)_3(CONHMe)(MeCN)_2 ,$$

was investigated, should also be mentioned. It is remarkable that, after a long reaction time, the amidine complex (CO_4). .$\overline{MnC(R'NMeCNHR)}$ is formed; the course of this reaction depends on the nature of the amine.

A comparatively stable carbamoyl complex of nickel, active in the carbonylation reaction, has been obtained recently:[186]

$$(Et_3NH)_2NiI_2 + CO \xrightarrow[THF]{Et_2NH} (Et_2NH)_2Ni(I)CONEt_2$$

It has been suggested that an unstable biscarbamoyl complex of nickel is formed on further treatment of the above compound with CO and Et_2NH.

Other questions associated with the formation and chemical reactions of carbamoyl complexes (metal-carboxylic acid amides) have been examined in reviews[187–189] (see the references therein); in the last study, certain aspects of the formation of alkoxycarbonyl complexes (metal-carboxylic acid esters) are examined in addition.

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As can be seen from the present review, metal-carboxylic acids and their derivatives constitute a fairly broad class of organometallic compounds. The interest in the synthesis of these complexes has increased still further in connection with the advances made in the field of the fixation of carbon dioxide in the presence of transition metal compounds. One of the aims of the present review was to attempt to demonstrate as far as possible the relation between these two trends in modern coordination chemistry.

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Table 4. Some X-ray diffraction data for metal-carboxylic acid amides.

Compound	Bond lengths, Å				OCN angle, deg	Refs.
	C=O	C–N	M–C	M–O		
$Mn(CO)_4(MeNH_2)CONHMe$	1.251	1.345	2.072	—	121.2	[8]
η^5-$CpMn(CO)(NO)CONH_2$	1.222 (6)	1.346 (6)	2.026 (4)	—	119.4 (3)	[167]
η^5-$CpW(CO)_3(MeNH_2)CONHMe$	1.25 (3)	1.41 (3)	—	—	113 (2)	[161]
$[NH_2(CHMe_2)_2][cis\text{-}PtCl_2(CO)CON(CHMe_2)_2]$	1.36 (3)	1.30 (3)	1.96 (2)	—	118 (4)	[178]
trans-$(Et_3P)_2Ni(I)CONEt_2$	1.237 (4)	1.359 (7)	1.882 (7)	—	120.7 (4)	[181]
$(Et_2NH)Ni_2I_2(\mu\text{-}CONEt_2)_2$	1.260 (6)	1.343 (8)	1.887 (5)	2.045 (4)	118.7 (5)	[181]
$HRu_3(CO)_{10}(\mu\text{-}CONMe_2)$	1.287 (4)	1.340	2.098 (8)	2.100 (5)	115.2 (7)	[182]
$Fe_2(CO)_6(\mu\text{-}AsMe_2)(\mu\text{-}CONMe_2)$	1.26 (2)	1.35 (2)	2.00 (1)	2.00 (1)	115.9 (11)	[183]
$[Fe(CO)_4(\mu\text{-}CONMe_2)]_2Ni$	1.285 (3)	1.334 (3)	2.001 (2)	1.855 (1)	115.8 (2)	[156]
$Fe(CO)_3CON(C_6H_{11})CPh{\cdots}CH{\cdots}CHPh$	1.22 (1)	1.39 (1)	1.978 (7)	—	124.5 (6)	[152]
$Mo(NO)(NCS)_4(\eta\text{-}CONMe_2)$	1.322 (7)	1.240 (10)	2.029	2.078	123.96	[184]
$Th(\eta\text{-}C_5Me_5)_2(Cl)(\eta^2\text{-}CONEt_2)$	1.44 (3)	1.34 (2)	2.418 (20)	2.460 (16)	108.9	[151]
$U(\eta\text{-}C_5Me_5)_2(\eta^2\text{-}CONEt_2)_2$	1.273	1.321	2.405 (8)	2.370 (5)	120.2	[151]

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Coordination Compounds of Transition Metals in the Chemistry of Aromatic Nitro-compounds

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The catalytic possibilities of coordination compounds of transition metals in the chemistry of aromatic nitro-compounds are discussed. The catalytic (including enzymic) reduction of aromatic nitro-compounds by various reductants, namely molecular hydrogen, alkali metal tetrahydroborates, CO + H_2O and CO + H_2 mixtures, alcohols, secondary amines, etc., is considered. The interaction of aromatic nitro-compounds with transition metal complexes, leading either to complexes containing the aromatic nitro-compound or to reduction products, is discussed. The structures of these complexes are classified. The bibliography includes 236 references.

CONTENTS

I. Introduction 419
II. Interaction of aromatic nitro-compounds with transition metal complexes 419
III. Reduction of aromatic nitro-compounds 422
IV. Enzymic reduction of aromatic nitro-compounds 427
V. Other reactions 428

I. INTRODUCTION

The chemistry of aromatic nitro-compounds is one of the traditional branches of organic chemistry in which considerable theoretical and practical advances have been achieved. Methods and technological processes, based on aromatic nitro-compounds, for the preparation of dyes, explosives, and medicinal preparations have been devised, considerable numbers of molecular complexes have been obtained, etc. At the present time an increased interest in compounds of this class has arisen. A characteristic feature in this instance is the invocation of ideas taken from coordination chemistry: the synthesis of new transition metal complexes incorporating aromatic compounds, the use of coordination compounds as catalysts in the reactions of aromatic nitro-compounds, etc. In this connection, it is useful to discuss new aspects arising in the interrelations between the chemistry of aromatic nitro-compounds and coordination chemistry.

Analysis of the literature has shown that the field of metal complex catalysis has been most fully investigated in relation to catalytic reactions such as the carbonylation and reduction of unsaturated hydrocarbons, deuterium–hydrogen exchange, and free-radical chain oxidation of aromatic compounds. The data on the interaction of aromatic nitro-compounds with transition metal complexes are scattered and have not been surveyed and there is no information about the reaction mechanism. Two recent reviews,[1,2] have been devoted to the reductive amination of aromatic nitro-compounds and their carbonylation with carbon monoxide,[1,2] data on their catalytic hydrogenation can be found in Refs.3–9, and those on their reduction by alkali metal tetrahydroborates have been published by Okushi.[10]

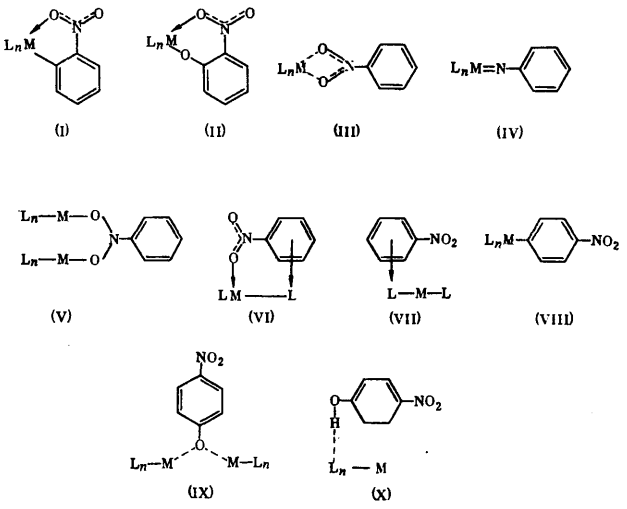
This review discusses the reactions of aromatic nitro-compounds with coordination compounds of transition metals and also the catalytic reduction of aromatic nitro-compounds by various reductants.

II. INTERACTION OF AROMATIC NITRO-COMPOUNDS WITH TRANSITION METAL COMPLEXES

The interaction of aromatic nitro-compounds with non-transition metal complexes (Al, Ga, Hg, etc.) leading to the formation of molecular complexes has long been known and has been investigated in fair detail.[11,18] In the main, the coordination of the metal to the oxygen (one or two atoms) of the nitro-group is postulated.

During the last several years, there has been an appreciable growth of interest in the reactions of aromatic nitro-compounds with transition metal complexes in connection with the elucidation of the mechanism of their catalytic action. Depending on the complex-forming ion, the ligand, and the reaction conditions, the interaction of aromatic nitro-compounds with transition metal complexes leads to the formation of either new stable complexes containing the aromatic nitro-compound (or its reaction product) in the coordination sphere or to organometallic compounds (metallation reaction).

Complexes in which the aromatic nitro-compound is coordinated in a wide variety of ways have been synthesised and to a large extent characterised. The types of compounds are presented below:



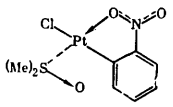
The structures indicated can be subdivided conventionally into two groups—in the first of these the nitro-group is linked to the metal and in the second the nitro-group does not participate in coordination of the aromatic nitro-compound to the metal. We shall not consider the interaction of coordination compounds with aromatic nitro-compounds where the nitro-group is fairly remote from the chelating or strongly accepting centres in the molecule and for this

reason does not participate in complex formation (see, for example, Refs.19–22).

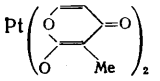
Complexes of type (I) have been formed via the reaction

$$PtCl_2(DMSO)_2 + RC_6H_4NO_2 \xrightarrow{\Delta} PtCl(DMSO)(RC_6H_3NO_2) + HCl + (DMSO).$$
$$R = H, p\text{-Me}, p\text{-Cl}.$$

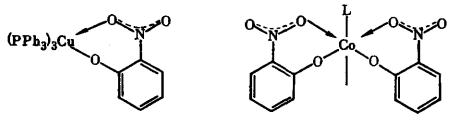
and isolated. The platinum atom has the planar coordination typical of platinum(II) and forms a five-membered ring with a molecule of the nitro-compound in which one of the oxygen atoms of the nitro-group and the carbon atom in the *ortho*-position to the nitro-group coordinate to platinum; the Pt–O and Pt–C bond lengths are 1.96 and 2.06 Å respectively:[23,24]



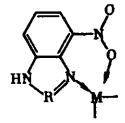
It has been shown by Raman spectroscopy that the nitro-group is coordinated to platinum in nitrobenzene solutions of the complexes[25] $PtCl_2(DMSO)_2$, K_2PtCl_4, and



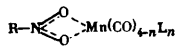
Complexes of type (II) have been isolated for copper, cobalt, and palladium.[26–29] A six-membered metallocycle is characteristic of these compounds, the metal atom are being linked to the oxygen atoms of the nitro- and hydroxy-groups:



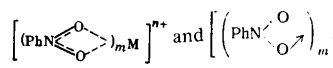
The nickel(II), copper(II), zinc(II), cadmium(II), and mercury(II) complexes of 4(7)-nitrobenzimidazole, investigated by IR, EPR, and electron spectroscopic methods, can be assigned to the same type.[30] It has been shown that these ligands are bidentate; the metal ions are coordinated to the oxygen of the nitro-group and the nitrogen of the imidazole ring with formation of a six-membered metallocycle:



The photolytic or thermal reaction of the pentacarbonylmanganese radicals with aromatic nitro-compounds in the presence of PBu_3 have been investigated by EPR.[31] A cyclic structure in which the manganese atom constitutes a bridge between two oxygen atoms of the nitro-group [type (III)] has been proposed on the basis of the EPR spectra of the stable paramagnetic species:

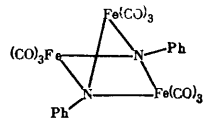


where R = t-butyl, isopropyl, phenyl, 3,5-dichlorophenyl, 2-thienyl, or 3-thienyl. The reactions of transition metal [Fe(III),[32] Co(II), Ni(II), Cu(II), Pd(II), and Mn(II)] chlorides[33] with $SbCl_5$ and aromatic nitro-compounds in an aprotic solvent (CCl_4) lead to the formation of complexes. $Fe(PhNO_2)_6(SbCl_6)_3$, $Fe(PhNO_2)_3(SbCl_6)_3$, and $FeCl(PhNO_2)_2(SbCl_6)_2$ are formed from the iron salt, complexes having the composition $M(PhNO_2)_2(SbCl_6)_2$ are produced from the cobalt, nickel, copper, and palladium salts, and the complex $Mn(Ph.NO_2)_3(SbCl_6)_2$ is formed from the manganese salt. The following structures have been assigned on the basis of spectroscopic studies:



The formation of nitrene derivatives [type (IV)] has been observed in many studies for the Co, Fe, Ru, Pd, Ti, V, Cr, Mo, and W complexes. A crystalline green product, to which the composition $Pd(acac)H(C_6H_5N=)Py$ was assigned on the basis of thermal and spectroscopic analyses, has been isolated.[34] The authors postulate the coordination of palladium to the nitrogen of the nitro-group with formation of a phenylnitrene complex.

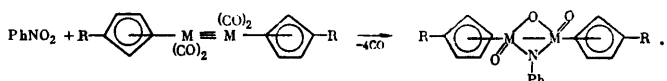
The interaction of nitrobenzene with $Fe_3(CO)_{12}$ in benzene containing methanol [35] or in a mixture of benzene, aqueous alkali, and a phase transfer catalyst,[36] leading to the reduction of nitrobenzene to aniline, has been investigated. A mechanism of the reduction process, involving the formation of intermediate nitrene complexes of iron, has been proposed. The compound



has been isolated and characterised. The authors suggest that the active species is the anion $HFe_3(CO)_{11}^-$. It has been shown that the IR spectra resembling those of the complex described above are observed when nitrobenzene (nitromethane [37]) is added in an He or H_2 atmosphere to the anion $HFe_3(CO)_{11}^-$ on an ion-exchange resin.[38] A similar mechanism has been put forward also for the reaction of nitrobenzene in tetrahydrofuran (THF) with titanium, molybdenum, and iron clusters having the composition $M_xC_4H_8$ ($x \geqslant 2$).[39]

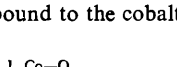
The study of the EPR spectra of the products of the interaction of $[Co(CN)_5]^{3-}$ and [(bis-salicylidene-ethylenediaminato)Co^{2+}] (salen) with an aromatic nitro-compound[40–43] demonstrated the presence of a cobalt nitroxide free radical or radical-anion in which there is a cobalt–nitrogen bond.

In order to investigate the mechanisms of the hydrogenation of aromatic nitro-compounds in the presence of ruthenium complexes, the products of the interaction of nitro-compounds with the complexes in the absence of hydrogen were isolated. Nitrene derivatives, whose structures have been shown to be $Ru_3(CO)_{10}NPh$ and $Ru_3(CO)_9(NPh)_2$ are isolated in an atmosphere of nitrogen after the reaction of nitrobenzene with $Ru_3(CO)_{12}$.[44,45] The same complexes can also be obtained by the reaction of aniline or phenyl isocyanate with ruthenium carbonyl. A reaction has been described in which the complex is fully decarbonylated:[46]



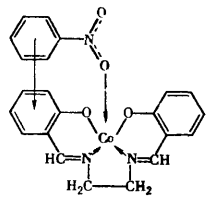
The yield is 40–46%. Hydrogenation of the reaction product under phase transfer conditions leads to the formation of an aromatic amine in a quantitative yield.

The formation of a dimeric compound on interaction of nitrobenzene with cobaloxime has been suggested,[47] the authors assuming that the nitro-group is bound to the cobalt atom via both oxygen atoms [type (V)]:



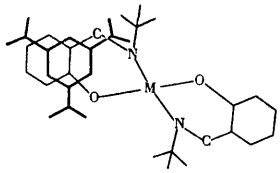
Thus stable complexes are obtained when both oxygen atoms of the nitro-group are coordinated to the metal atom. When the nitro-group is coordinated via one oxygen atom, the complexes are stabilised via the formation of a metallocycle incorporating a ring carbon atom in the *ortho*-position relative to the nitro-group or the oxygen atom of the hydroxy-group. Nitrene complexes with a metal–nitrogen bond are stable.

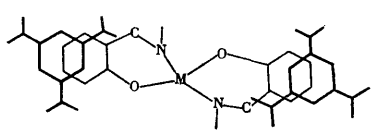
The interaction of aromatic nitro-compounds with cobalt and copper complexes (in which Schiff bases are ligands) has been investigated.[48] It has been shown that the reaction product is characterised by a high-intensity band in the electronic spectra in the range 420–432 nm. A black adduct of Co^{2+}(salen) with nitrobenzene, in which the aromatic ring of nitrobenzene is located above the plane of the ligand and in which the oxygen atom of the nitro-group is linked to the metal [type (VI)], has been isolated:



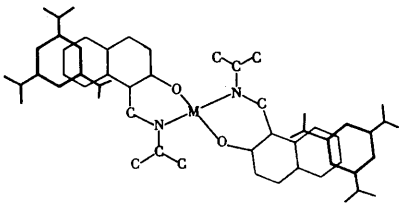
In the complex bis(*N*-*p*-nitrophenylsalicylaldiminato)Cu(II).dioxan, the copper atom is coordinated via four atoms (two oxygen atoms and two nitrogen atoms) of the ligands as a chelate and two monomeric complexes, linked via the centre of symmetry, give rise to a dimer as a result of the formation of a strong axial Cu...O bond. The coordination of the copper atom is built up to a distorted octahedral form via the oxygen atom of the nitro-group, which leads to the formation of an infinite polymer chain.[49]

Many complexes containing highly conjugated ligands—porphyrins, dyes, *o*-hydroxyquinones, and 8-hydroxyquinolines—form donor–acceptor complexes with aromatic nitro-compounds, in which there is no metal–nitro-group bond [type (VII)] ("peripheral mechanism"). The interaction of tetra-*p*-tolylporphyrinatocobalt(II),[50,51] palladium(II), cobalt(II), copper(II), and nickel(II) 5,10,15,20-tetraphenylporphyrinates[52–54] and the dimethyl esters of the meso-porphyrin complexes of cobalt(II) and nickel(II) [55] with 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone has been investigated and it has been shown that, under these conditions, the $\pi-\pi$ interaction takes place exclusively on the periphery of the porphyrin and does not involve the metal. X-Ray diffraction studies have demonstrated that *sym*-trinitrobenzene forms 1:1 [56] and 1:2 [57] compounds with M^{2+} complexes of bis-salicylidene-ethylenediamine (salen) and is located exclusively over the π-system of the ligand, the planes of the two ligands being parallel. A similar interaction has been described[58–64] for copper(II) and palladium(II) 8-hydroxyquinolinates with a series of strong acceptors: *sym*-trinitrobenzene, chloranil, etc. In the donor–acceptor complexes formed, the acceptor is localised exclusively over the donor and is not linked to the metal atom:

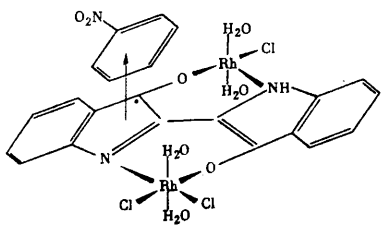




Molecular complexes of 1,3,5-trinitrobenzene with copper(II), nickel(II), and palladium(II) 1-alkylaminomethyl-2-naphthoxides have been synthesised.[65] The structure of the adduct of palladium(II) 1-isopropylaminomethyl-2-naphthoxide with trinitrobenzene has been investigated by X-ray diffraction. The plane of the nitro-compound is parallel to that of the naphthalene ring and trinitrobenzene is disposed over the terminal naphthalene ring:



The interaction of nitrobenzene, a week acceptor, with coordination compounds of transition metals has been studied in a number of investigations. It has been shown that nitrobenzene reacts with haematoporphyrin to form a weak 1:1 complex.[66] Stoichiometric reduction of nitrobenzene by the rhodium(II)–potassium indigo-sulphonate complex in solution[67] proceeds at the expense of the electrons of both the ligand and rhodium(II). A signal whose intensity corresponds to 2–3% of paramagnetic species relative to the amount of the complex has been detected in the EPR spectrum on interaction of nitrobenzene with this complex bound to alumina. The mechanism of the activation of nitrobenzene involves the intermediate formation of a peripheral complex via the π orbitals of the ligand and nitrobenzene:



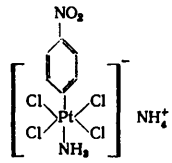
The formation of molecular complexes between nitrobenzene and copper(II) bisalizarinate has been demonstrated by ^{1}H NMR.[68] The nitro-group in the molecular complex is oriented towards the side opposite to that of the copper(II) ion. It has been demonstrated by electronic emission spectroscopy[69] that the character of the interaction of alizarin and palladium bisalizarinate with an aromatic nitro-compound is isotypical which led the authors to the conclusion that the interaction of the nitro-compound with a palladium complex has a peripheral mechanism.

In the 1:1 donor–acceptor complex of the tricarbonylchromanisole and *sym*-trinitrobenzene,[70] there is interaction between the aromatic systems of the nitro-compound and the complex. The planes of anisole and trinitrobenzene form a small angle of 3° and the centres of the planes are somewhat displaced relative to one another, so that the interaction in this system is weaker than between the aromatic systems without the metal.

A specific "metal ion–nitrobenzene" interaction via the hydrogen bond of the NH protons has been observed in a study of the electrical conductivity of [Co(acac)$_2$diamine]X in nitrobenzene.[7,72] Furthermore, there is $\pi-\pi$ interaction in this system between the bipyridyl ligand and the nitrobenzene molecule.

As can be seen from the data presented, a strong $\pi-\pi$ interaction between the aromatic system of the nitro-compound and the highly conjugated ligand is characteristic of complexes of this group [types (VI) and (VII)], the nitro-group either not being involved in complex formation or being additionally coordinated to the metal ion via the oxygen atom.

Complexes of type (VIII) have been isolated after the reaction of nitrobenzene or *p*-nitrotoluene with H_2PtCl_6 in $CF_3COOH-H_2O$. The isomers of the *m*- and *p*-σ-aryl complexes of platinum(IV) were obtained in which the nitro-group does not enter the coordination sphere of platinum:[73]



Nitrophenol can serve as a bridge between two copper atoms [type (IX)], the authors indicating that the IR spectra of structures of type (II) and (IX) do not differ.[27] In the 1 : 1 adduct of *p*-nitrophenol and Cu^{2+}(salen), nitrophenol is disposed between the molecules of the chelate.[74] The oxygen atom of the phenol forms a hydrogen bond with the oxygen of the donor and this adduct is linked solely to the ligand and not to the metal atom. The nitrogroup does not participate in the binding to the chelate [type (X)]. A polymeric nitrobenzene complex of nickel stable in air has been isolated:[75]

$$NiO_2(t\text{-BuNC})_2 + PhNO_2 + t\text{-BuNC} \rightarrow Ni(PhNO_2)(t\text{-BuNC})_2.$$

Table 1. Interaction of aromatic nitro-compounds with transition metal complexes.

No.	Aromatic nitro-compound	Metal ion	Type of compound	Method of investigation*	Refs.
1	Nitrobenzene, *p*-nitrotoluene, *p*-chloronitrobenzene	Pt(II)	(I)	RRS, XRD	[23—25]
2	*o*-Nitrophenol, Nitrobenzimidazole	Cu(II), Co(II), Pd(II), Ni(II)	(II)	IR, EPR, XRD	[26—30]
3	Nitrobenzene, 3,5-dichloronitrobenzene, α-nitronaphthalene	Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Pd(II)	(III)	IR, EPR	[31—33]
4	Nitrobenzene	Co(II), Fe(III), Ru(II), Pd(II), Mo(II), Cr, Fe	(IV)	XRD, IR, EPR	[34—46]
5	Nitrobenzene	Co(II)	(V)	IR	[47]
6	Nitrobenzene	Co(II), Cu(II)	(VI)	IR	[48, 49]
7	1,3,5-Trinitrobenzene, 2,4,7-trinitrofluorenone	Co(II), Pd(II), Cu(II), Ni(II), Cr(III)	(VII)	^{1}H NMR, XRD	[50—65, 70]
8	Nitrobenzene	Rh(II), Cu(II), Pd(II), Co(II)	(VII)	EPR, ^{1}H NMR, EES	[66—69, 71, 72]
9	Nitrobenzene, *p*-nitrotoluene	Pt(IV)	(VIII)	XRD, ^{1}NMR	[73]
10	*o*-Nitrophenol	Cu(II)	(IX)	IR, XRD	[27]
11	*p*-Nitrophenol	Cu(II)	(X)	XRD	[74]

*RRS = resonance Raman spectroscopy, XRD = X-ray diffraction analysis, and EES = electronic emission spectroscopy.

The complex $Ni(PhNO_2)_2(PPh_3)_2$ has been obtained in the form of crystals.

Table 1 compiles data on the formation of complexes by aromatic nitro-compounds with transition metal complexes.

III. REDUCTION OF AROMATIC NITRO-COMPOUNDS

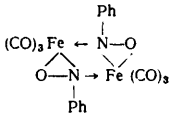
1. Reduction by Transition Metal complexes

Numerous studies have been devoted to the reduction of aromatic nitro-compounds by metal complexes. The iron carbonyl cluster $Fe_3(CO)_{12}$ possesses reducing properties in benzene, hexane, and THF. In methanol-containing benzene, mixing of an equimolar amount of nitrobenzene and $Fe_3(CO)_{12}$ leads to the formation of an aniline.[35] The rate of reaction can be increased by an order of magnitude by introducing a phase transfer catalyst.[36] In a CO atmosphere, an aniline is also the reaction product.[66] The use of this cluster on alumina lowers the selectivity of the reaction; a mixture of an aniline and azobenzene is obtained, the yield of anilines depending on the substituent in the aromatic ring and varying in the range 40—79%, while the yield of azobenzene does not exceed 4—7%.[77] The reducing species is the $HFe_3(CO)_{11}^-$ anion,[78] which can be obtained in its turn by treating $Fe_3(CO)_{12}$ in THF with 1 M tetrabutylammonium fluoride solution. If this reaction is carried out in the presence of *p*-nitrotoluene, *p*-toluidine is detected. Furthermore, this anion can be isolated from the reaction

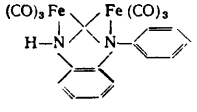
$$Fe_3(CO)_{12} + KF + 18\text{-crown-6} \rightarrow [HFe_3(CO)_{11}]^-.$$

When manganese pentacarbonyl was treated with $(C_4H_9)_4NF$ or $(C_4H_9)_4NF.3H_2O$, its anion was obtained. It reduces nitrotoluene and nitroanisole to the corresponding anilines in the presence of water in 52—88% yield. The corresponding cobalt compound does not reduce the aromatic nitro-compounds.

Iron pentacarbonyl, in the presence of which aromatic nitro-compounds are reduced to nitroso-compounds, is extremely reactive. The nitroso-compounds subsequently form a complex with the iron. Thus a nitrosoiron complex was isolated from a mixture of 3-chloro-2-methylnitrobenzene with $Fe(CO)_5$ and its structure was determined:[79]



Monomeric or dimeric iron complexes are formed in the reduction of iron pentacarbonyl under the influence of light or ^{60}Co γ-radiation.[80] It has been stated that under other conditions one mole of nitrobenzene can be reduced by one mole of iron pentacarbonyl to azoxybenzene and 1.4 mole is reduced to azobenzene in yields up to 76%. Treatment of nitrobenzene with a large excess of iron pentacarbonyl in hot butanol or with 1.4 mole of iron nonacarbonyl can yield the complex



The reaction of $KHFe(CO)_4$ with nitrobenzene at room temperature takes place exothermically, CO_2 is evolved, and the reaction product is aniline.[81] If bromomagnesioalkyl- or bromomagnesioarylamides are added to the reaction mixture, the reaction products are asymmetric *NN'*-disubstituted ureas (yield 42—99%):[82]

$$R'NHMgBr + Fe(CO)_5 + R^1NO_2 \rightarrow R'NHCONHR^1.$$

It has been suggested that carbamoyltetracarbonylferrate is formed initially and then reacts further with the aromatic nitro-compound.[83]

The interaction of acyltetracarbonylferrates with nitrobenzene[83] leads to anilines. Ferrates are both reducing and acylating agents:

$$R'COFe(CO)_4^- + PhNO_2 \rightarrow R'CONHPh\ .$$

The yield of the target products is 68–86% and the amine R′NHPh is a side product.

The mechanism of the oxidation of the iron-porphyrins by an aromatic nitro-compound has been studied:[84,85]

$$6Fe^{II} + PhNO_2 + 6H^+ \rightarrow 6Fe^{III} + PhNH_2 + 2H_2O\ .$$

The rate of reaction diminishes in the sequence trinitro > dinitro > mononitro. Aromatic nitro-compounds are then reduced to amines, whose yield falls appreciably when various substituents are introduced into the aromatic ring. Comparison of iron-porphyrins with haemoproteins showed that the latter exhibit a very low activity. This effect is associated, according to the authors, with the fact that the rate-limiting stage is the dissociation of the protonated aromatic nitro-compound (by analogy with the mechanism of the oxidation of iron-porphyrins by molecular oxygen[86]). The aromatic nitro-compound interacts directly with the iron atom, although in the presence of a solvent such as pyridine one cannot rule out the possibility of a peripheral mechanism.

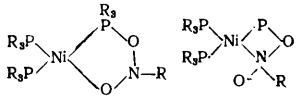
The reaction of *o*-nitrophenol with $[Ru(CO)_3(PPh_3)_2]$ (which is a catalyst of the hydrogenation of aromatic nitro-compounds[107]) takes place in an interesting manner. A ruthenium complex has been isolated[87] in which one nitrophenol molecule is bound to ruthenium via the oxygen atom of the OH group while the other has been transformed into a nitroso-derivative and has been coordinated to ruthenium via the nitrogen of the nitroso-group and the oxygen of the OH group. The nitro-group is not coordinated to ruthenium and is not coplanar with the benzene ring. Complexes of zerovalent nickel also reduce aromatic nitro-compounds to the nitroso-derivatives;[88] the reaction takes place rapidly in benzene with a sharp change in colour:

$$PhNO_2 + Ni(PPh_3)_4 \rightarrow (PhNO)Ni(PPh_3)_2 + OPPh_3 + PPh_3\ .$$

In the presence of nickel complexes, oxygen is transferred from the aromatic nitro-compound to the phosphine in accordance with the following scheme:

$$NiL_4 \rightleftharpoons NiL_3 + L\ ,$$
$$NiL_3 + RNO_2 \rightarrow [Ni^{I}L_3 \cdot RNO_2^-]\ ,$$
$$[Ni^{I}L_3 \cdot RNO_2^-] \rightarrow L_2Ni(ONR) + LO\ .$$

The formation of intermediate complexes with nitrobenzene is then postulated:



When 3,4-dichloronitrobenzene is added to a solution of the $NaBH_4$-treated iridium(IV) complex of chloranilic acid, the 3,4-dichloronitrobenzene radical-anion is formed.[89]

Metal-chelated flavins reduce the aromatic nitro-compound, the reducing property depending on the metal ion and increasing in the sequence Mn(II) < Zn(II) < Ni(II) < Co(II).[90]

Table 2 presents data on the reduction of aromatic nitro-compounds by transition metal complexes.

In conclusion we may note general characteristics. Aromatic nitro-compounds are reduced via the formation of the nitro-compound radical-anion with subsequent reduction to the nitroso-compound. Depending on the complex-forming metal, the nitroso-compound can subsequently give rise to a stable complex with the metal (iron, nickel, cobalt, ruthenium) or it can be reduced with formation of various products (iron).

2. Reduction by Molecular Hydrogen

It is known that the reduction of aromatic nitro-compounds can lead to a series of products:

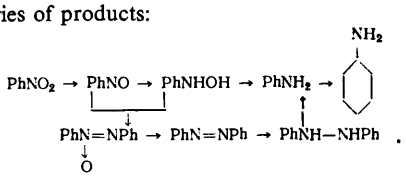


Table 2. Reduction of aromatic nitro-compounds by metal complexes.

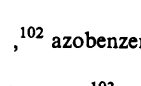
No.	Complex	Aromatic nitro-compound	Reaction products	Remarks	Refs.
1	$Fe_3(CO)_{12}$	Nitrobenzene	Aniline	—	[35,36, 76]
2	$Fe_3(CO)_{12}$	Substituted nitrobenzenes	Substituted anilines, azobenzenes	Complex on Al_2O_3	[77]
3	$Fe_3(CO)_{12}$	*p*-Nitrotoluene	*p*-Toluidine	Addition of tetra-butylammonium fluoride or KF + crown-ether	[78]
4	$Mn_2(CO)_{16}$	ditto	ditto	Ditto	[78]
5	$Fe(CO)_5$	3-Chloro-2-methyl-nitrobenzene	Nitrosoiron complex	—	[79]
6	$Fe(CO)_5$	Substituted nitrobenzenes	Ditto	Under the influence of light or ^{60}Co γ-rays	[80]
7	$Fe(CO)_5$	Substituted nitrobenzenes	*NN*′-disubstituted ureas	Addition of RNHMgBr	[82]
8	$Fe(CO)_4(RCO)$	Nitrobenzene	Amide, amine	—	[83]
9	Iron-porphyrins	Mono-, di-, and tri-nitrobenzenes	Anilines	—	[84, 85]
10	$Ru(CO)_3(PPh_3)_2$	*o*-Nitrophenol	Nitronitroso-ruthenium complex	—	[87]
11	$Ni(PPh_3)_4$	Substituted aromatic nitro-compounds	Nitroso-compounds of nickel	—	[88]
12	Ir(CAA)* + $NaBH_4$	3,4-Dichloro-nitrobenzene	3,4-Dichloronitro-benzene radical-anion	—	[89]
13	Flavin radicals containing manganese, nickel, and cobalt	Substituted aromatic nitro-compounds	Radical-anions of aromatic nitro-compounds	—	[90]

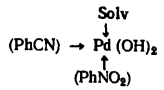
*CAA = chloranilic acid.

The study by Ogata and Sugiyama[91] may be regarded as the first of this kind, but vigorous research has been prosecuted mainly during the last 20 years. One of the first catalysts used in this reaction is cobalt pentacyanide. In aqueous[92] and aqueous alkaline[93,94] solutions close to room temperature, the product of the halogenation of nitrobenzene is azobenzene,[92] while the halogenation of nitrobenzen and *o*-nitroanisole results in a mixture of azo- and hydrazo-compounds,[93] while at elevated H_2 pressures a mixture of an amine and an azo-compound is produced.[94] Complexes of bisdimethylglyoximatocobalt(II) catalyse the hydrogenation of aromatic nitro-com pounds under mild conditions to an aniline and hydrazobenzene an the hydrogenation of methyl *p*-nitrocinnamate to methyl *p*-amino-cinnamate in 78% yield.[95] When nitrobenzene is reduced in the presence of cobalt pentacyanide, the rate of reaction depends on th

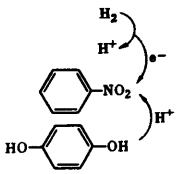
OH^- concentration and the catalyst : substrate ratio; thus, when the ratio of cobalt to nitrobenzene is less than unity, the reaction does not occur. In an aqueous alcoholic medium with added KOH, the reaction products are azo- and azoxy-benzenes.[96]

Cobaloximes having the composition $Co(DMG)_2OAc$ and $[Co(DMG)_2]_2CO_3$, where DMG = dimethylglyoxime, are more active catalysts.[97] The catalytic activity is manifested only in the presence of an amine, for example, morpholine. In a mono-olefin–nitrobenzene mixture, the latter is hydrogenated selectively,[98] while isoprene fully inhibits the reaction. It has been suggested that the hydrogenation proceeds via an intermediate dinuclear complex.[99] The presence of a stronger base (KOH, NaOH) is necessary for the manifestation of catalytic activity by the complex (DMG) $(PPh_3).XCo^I.C_2H_5OH$ (X = Cl or Br).[100] At elevated hydrogen pressures, the reaction takes place also in the absence of a base. In contrast to the previously study, Datta et al.[100] suggest that the hydrogenation takes place via the formation of an intermediate phenylnitrene complex. The copper complex $Cu^IBr(PPh_3)_3$ is active under severe conditions.[101] The nitrobenzene halogenation products are aniline (75–79%), azobenzene (5–10%), and nitrosobenzene (2–7%). It has been shown that in an atmosphere of hydrogen the initial complex is transformed into the hydride complex $[CuHBr(PPh_3)]_2$, while at the end of the reaction the complex $(PhN=NPh)Cu_2(PPh_3)_4Br_2$ was isolated.

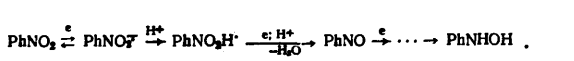
Palladium and platinum complexes are more active and selective. Under mild conditions, nitrobenzene was hydrogenated to aniline (98%) in the presence of the $NaBH_4$-treated complex PdL_2Cl_2 (where  , [102] azobenzene, and pyridines[103]). Hydrazobenzene [102] or azobenzene [103] may be present as impurities. A high yield of aniline was obtained also in the presence of the $Pd(PhCN)_2Cl_2$ catalyst.[104] At elevated hydrogen pressure, the yield of aniline falls to 65%.[105] New bands appeared in the electronic and infrared spectra after the addition of nitrobenzene to the complex, which the authors attributed to an intermediate complex having the composition



The mechanism of the reduction of nitrobenzene in an aprotic solvent (DMSO) in the presence of the $PtCl_2(DMSO)_2$ + $NaBH_4$ catalyst and added quinones has been investigated.[106] Under the hydrogenation conditions, the quinones are rapidly and quantitatively reduced to hydroquinones, which facilitates the reduction of nitrobenzene as a result of the protonation of the intermediate reduction products. The function of the catalyst consists in electron transfer from H_2 to nitrobenzene, while the role of the hydroquinone, introduced into the system or formed on hydrogenation of quinone, is to transfer a proton. The formation of donor–acceptor complexes of nitrobenzene with hydroquinone has been postulated:

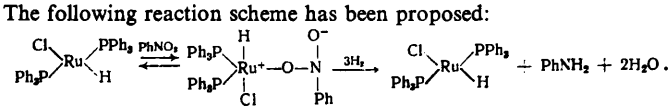


The reduction of nitrobenzene is described by the scheme



The final hydrogenation product is phenylhydroxylamine.

The ability to catalyse the selective reduction of dinitrobenzenes to the corresponding nitroanilines is a unique feature of ruthenium complexes.[107–109] Substituted nitrobenzenes are hydrogenated only at the nitro-group (in the presence of ruthenium and iron complexes). The following reaction scheme has been proposed:



Here one can imagine that the stage involving the interaction with the nitro-compound is more complex (see, for example, Pizzotti and Crotti[87]). The iron complexes are less active. The complex $RuCl_2.(PPh_3)_3$ exhibits the highest specificity in the hydrogenation of dinitrobenzene to nitroanilines,[107,110] which permitted the selective hydrogenation of mixtures of dinitro- and nitro-compounds. For example, in a mixture of nitrobenzene with *p*-dinitrobenzene, only *p*-dinitrobenzene is reduced (to *p*-nitroaniline).[111] *o*-Substituted nitro-compounds are more effectively hydrogenated in the presence of a quaternary ammonium base and ruthenium(II) and ruthenium-(III) complexes;[112] alcohols, halogenohydrocarbons, or ethers can serve as solvents. The selectivity with respect to reaction products is 85% for a 95% conversion.

The dimeric ruthenium hydride, obtained from $RuCl_2.(\eta^6\text{-}C_6Me_6).(PPh_3)$ and Na_2CO_3 in isopropyl alcohol, shows a low catalytic activity in the hydrogenation of nitrobenzene; the yield of aniline reaches 38% after 36 h at 50 °C and 50 atm.[113]

The titanium(III) compounds obtained by reducing the titanium-(IV) compounds $R_nTi^{IV}Cl_{4-n}$ (where R = $MeCOO^-$, PhH_2COO^-, or $\alpha\text{-}C_{10}H_7CH_2COO^-$; n = 0, 1, 2) with hydrogen catalyse the hydrogenation of nitrobenzene to aniline in the presence of heterogeneous catalysts in dimethylformamide (DMF).[11]

Wilkinson's complex $RhCd(PPh_3)_3$ is inert in the hydrogenation of aromatic nitro-compounds. When a phosphine or an amine is added to the reaction medium, nitrobenzene is hydrogenated to aniline at a low rate (0.2–2.6 moles of H_2 per mole of rhodium per minute).[115–117] Under the same conditions, the rhodium complex Rh(hexa-1,5-diene)Cl_2 catalyses the reduction of substituted nitro-compounds, appreciable dehalogenation being observed for halogeno-derivatives.[116] The complex $RhPy_3Cl_2$, which manifests a catalytic activity after treatment with $NaBH_4$ and DMF, has been studied in detail.[115,118,119]. The intermediate catalytically active complex $Py_2.(DMF)RhCl(BH_4)$ was isolated. It was noted that the catalyst decomposes after a time owing to the reduction of the ligand—pyridine. The dinuclear rhodium complexes with a bridging nitrogen heterocycle, namely [(COD)ClRh(μN–N)RhCl(COD)], where COD = cyclo-octa-1,5-diene or *NN'*-bipyridyl, are more stable.[120,121] After treatment with $NaBH_4$, the complexes catalyse the hydrogenation of nitrophenols and nitrobenzoic acid. The authors did not characterise the active species.

The catalytic activity of sulphur-containing rhenium complexes has been investigated in a number of studies. At 95 °C and 1–40 atm H_2, nitrobenzene and *o*-nitrotoluene were hydrogenated to the corresponding anilines in the presence of complexes with thiourea or mercaptobenzimidazole $[ReOL_2X_3].2H_2O$;[122] the rhenium thio-complexes $Re_2S_2L_8$, where L = $CS(NH_2)_2$, Cl^-, or H_2O, catalyse the conversion of nitrobenzene to azoxybenzene in DMF.[123,124]

Metal clusters have been investigated in recent years as catalysts. The palladium cluster $Pd_5(PPh)_2$ in DMF,[125] the complex obtained by the interaction of the platinum cluster $[Pt_3Sn_8Cl_{20}]^{4-}$ with cyclo-octa-1,5-diene and having the composition $(C_6H_{12})_3Pt_3Sn_2Cl_6$,[126] and soluble polynuclear rhenium thio-complexes[124] catalyse the hydrogenation of nitrobenzene under mild condtions. The reaction has been investigated potentiometrically[126] and it has been shown that the platinum is in the zerovalent state. At temperatures in the range 100–130 °C and pressures in the range 100–300 atm, the iron

cluster $[(\eta^5\text{-}C_5H_5)Fe(\eta^3\text{-}CO)]_4$, in which each iron atom is linked to three other iron atoms and three carbonyl ligands, is active; the yield of aniline is 6–31%.[127]

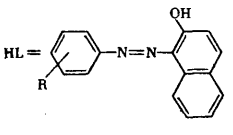
Catalysts obtained by immobilising complexes (mainly palladium and platinum) on carriers have been used successfully. Palladium complexes with polyvinylpyrrolidinone and polyacrylic acid fixed on silica gel,[128] the $Pd(PPh_3)_n^{2+}$ complex on organic and inorganic carriers,[129] the palladium(II) complex on γ-aminopropyl-containing silica gel,[130] and palladium complexes with chloromethylated polystyrene treated with anthranilic acid,[131–133] with a polymeric carrier containing oxime groups,[134,134] with polymeric ligands containing NH groups in the polymer chain,[136–138] etc. have a high activity in the hydrogenation of aromatic nitro-compounds. The main reaction products are the corresponding anilines. Dinitro-compounds can be hydrogenated stepwise with isolation of the mononitro-compounds.[130] It has been noted that the hydrogenation of *p*-chloronitrobenzene is accompanied by dehalogenation.[132] The platinum-nylon catalyst, familiar in the selective hydrogenation of benzene to cyclohexene, hydrogenates nitrobenzene and its derivatives in the liquid phase.[139]

The most active catalysts in the reduction of aromatic nitro-compounds are complexes based on platinum-group metals with highly conjugated ligands (arylazonaphthols, azobenzene, *o*-quinones, *o*-hydroxyquinones, γ-indigoid dyes). The reactivity of the majority of the catalysts which were described is associated with the non-complementary character of the process. The intermediate metal hydride complex is a two-electron reductant, while nitro-compounds are one-electron acceptors.

In complexes incorporating ligands with a branched system of π-bonds, there is a possibility of electron transfer via a peripheral mechanism through the ligand.[5,140] At the beginning of our review, the list of such complexes is given in which donor–acceptor interaction takes place between the aromatic nitro-compounds and the highly conjugated ligand (Table 1). The use of catalysts of this kind made it possible to achieve effective and selective hydrogenation of aromatic nitro-compounds under mild conditions:[141–143]

$$RC_6H_4NO_2 \rightarrow RC_6H_4NHOH\ (96—99\%),$$
$$RC_6H_4NO_2 \rightarrow RC_6H_4NH_2\ (100\%),$$
$$C_6H_4(NO_2)_2 \rightarrow H_2NC_6H_4NO_2\ (95—98\%),$$
$$ClC_6H_4NO_2 \rightarrow ClC_6H_4NH_2\ (99{,}9\%).$$

N-Arylhydroxylamines have been synthesised in 96–99% yield in the presence of the platinum complexes $Pt_2L_3(HL)Cl$, where



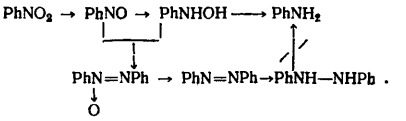
R = H, 4-Me, 2,4-$(Me)_2$, or 4-SO_3Na and L are the corresponding benzeneazonaphthoxides [144–148] or PtQ_2 (where Q = *o*-hydroxyquinones).[149] Platinum complexes with azobenzenes exhibit a lower selectivity (the yield of *N*-phenylhydroxylamine is 55%).[150] The corresponding palladium complexes of azobenzenes[151] are more active then the platinum complexes.[57,150] The reaction takes place via the formation of phenylhydroxylamine, but the final product is aniline. Palladium complexes of *o*-hydroxyquinones[152] and platinum complexes of *o*-γ-pyrone and *o*-quinone[103] are effective catalysts of the hydrogenation of aromatic nitro-compounds to anilines. The reduction of dinitrobenzenes to mononitro-derivatives is catalysed by platinum and palladium complexes of *o*-hydroxyquinones[153,154] and the reduction of halogenonitrobenzenes to the corresponding halogenoanilines (without the occurrence of the dehalogenation side reaction) is catalysed by platinum, rhodium, and iridium complexes.[155–159]

Thus the synthesis and use of complex catalysts containing as ligands large conjugated systems with a considerable electron capacity constitutes an extremely fruitful and promising development.

3. Reduction by Alkali Metal Tetrahydroborates

The reduction of aromatic nitro-compounds by alkali metal tetrahydroborates in water and aqueous alcoholic solution of alkali is known to lead to the $PhNO_2^-$ radical-anion,[160] while the reaction in diglyme at elevated temperatures affords azoxybenzene.[161] Transition metal complexes catalyse the reduction process. The cobalt complexes have been most thoroughly investigated.

The reduction of nitrobenzene by $NaBH_4$ in the presence of cobaloxime $H-Co(DMG-H_2)(PPh_3)$ on heating in 50 alcoholic solution was first observed by Sal'nikova and Khidekel'.[162] Nitrobenzene was reduced quantitatively to a mixture of azobenzene (30%), azoxy-benzene (60%), and aniline (10%). The same mixture was obtained in the presence of the complex $H-Co(DMG-H_2)Py$.[151,163] Nitrobenzene and the products of its incomplete reduction have been reduced[164] with sodium and potassium tetrahydroborates in the presence of cobalt(III) complexes—cobalt bisguanide, the cobalt–salen complex, and the cobalt complex of a macrocyclic Schiff base. The complexes were compared with vitamin B_{12} and its model—the cobalt bisdimethylglyoximate complex. The general characteristic of the systems investigated have been discovered: the Co^{3+} ion is reduced to Co^+ or the cobalt(III) hydride; Co^{2+} interacts weakly and Co^+ and the hydride interact strongly with the substrate. The reaction proceeds mainly in the forward direction: nitrobenzene → nitrosobenzene → phenylhydroxylamine → aniline. Among the side products, azoxy- and azo-benzenes were detected, ar increase in the reaction temperature from 40° to 100 °C resulting in an increase in the yield of aniline. The same features have been observed when hydroxycobalamin was used as the catalyst.[165] It has been suggested that the catalytic system involves the formation of an unstable cobalt–nitrogen intermediate compound (nucleophilic addition to an unsaturated system). On the basis of kinetic measurements, the following reaction mechanism has been put forward:[165]



Cobalt(II) compounds are also active. The first stage is probably the reduction by alkali metal tetrahydroborates of cobalt(II) to cobalt(I), which is in fact the active catalytic species. The composition of the product varies markedly as a function of the nature of the ligand and the solvent. Thus in methanol in the presence of $Co(II)-Co(DMG)_2$, $CoCl_2$, $Co(AcO)_2$, etc., hydrazobenzene and aniline were obtained,[166] in the presence of the Co(II)–mesoporphyrin complex the products were phenylhydroxylamine (34%) and azoxybenzene (35%),[167] while in the presence of the complexes $Co(bipy)_3^+$ and $Co(bipy)_3^{3+}$ the products were phenylhydroxylamine and aniline.[168] The last two cobalt complexes react rapidly with the tetrahydroborate to form a cobalt(I) complex. The nitrile group is reduced faster than the nitro-group, which enabled the authors to carry out the selective reduction of *p*-nitrobenzonitrile to *p*-nitrophenylmethylamine at –10 °C in the presence of the $CoCl_2 + NaBH_4$ system.[169] On raising the temperature, the nitro-group is also reduced.

The highest yield of aniline has been achieved in the presence of the $CuCl_2 + NaBH_4$ catalytic system.[170] In the series of metal acetylacetonates, the highest activity is manifested by copper acetylacetonate,[171] in the presence of which the yield of aniline reaches 90%.

Nickel complexes are active in an inert atmosphere. In water at 70 °C in the presence of cyanonickel complexes,[172] nitrobenzene is readily reduced to azoxybenzene. In an alcoholic medium under the

same conditions in the presence of the $Ni(PPh_3)_2Cl_2$ complex, substituted nitrobenzenes are reduced to the corresponding anilines in 80–88% yield.[173] The reaction selectivity changes sharply when nickel complexes fixed on polymers containing PPh_2 or CH_2PPh_2 groups on the surface are used—the main product is azoxybenzene (up to 85%) with an admixture of azobenzene.[174]

Rhodium(III) complexes, which form hydrides, for example, the hydridochlorotriethylenetetra-aminerhodium(III) cation, catalyse the reduction of nitrobenzene to aniline in solution in aqueous methanol.[175] It is noteworthy that the reduction of aromatic nitro-compounds by alkali metal tetrahydroborates has not found extensive application owing to the low activity and selectivity.

4. Reduction by the Synthesis Gas

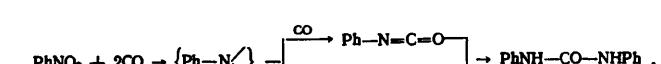
Although the first communication about the reduction of aromatic nitro-compounds by the CO + H_2 mixture in the presence of iron pentacarbonyl appears in 1925,[176] studies in this field were initiated much later. Virtually all the investigations demonstrated that catalytic activity is manifested by transition metal carbanions. The complexes $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ [177,178] in benzene or a benzene–alcohol mixture at 120 °C and 100 atm CO + H_2 catalyse the reduction of nitro-compounds to amines in 94–100% yield:

$$PhNO_2 + 2CO + H_2 \rightarrow PhNH_2 + 2CO_2 .$$

Diphenylurea is a side product (5–6%).

In the presence of cobalt carbonyl, *p*-nitrobenzyl alcohol is reduced to a polymer of *p*-aminebenzyl alcohol (44%), while nitrobenzene is reduced to acetanilide (44%).[179] These results can be explained by the presence of acetic acid (obtained as a result of hydrolysis on synthesis of cobalt carbonyl from cobalt acetate); aniline has not been detected. The reduction of nitrobenzene, *m*-dinitrobenzene, and 2,4-dinitrotoluene under hydroformylation conditions is catalysed by rhodium, iridium, iron, and osmium carbonyls. Iron carbonyl is the least active, while osmium carbonyl is active even in the absence of hydrogen.[180] The yield of the amino-product is 97%. The low activity of iron pentacarbonyl has also been indicated by L'Esplattenier et al.[181]

Ruthenium(III) complexes, namely ruthenium dodecacarbonyl, ruthenium pentacarbonyl, and trisacetylacetonatoruthenium, are active catalysts. Urea was detected among the products for the $C:H_2 > 1$ ratio, its amount increasing with increase in the quantity of CO in the mixture. It has been suggested that a phenylnitrene complex is an intermediate:[181]

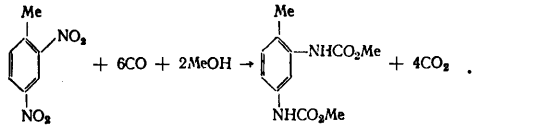


The introduction of sodium methoxide into the reaction medium alters the course of the reaction:

$$PhNO_2 + CO + H_2 + NaOMe \xrightarrow{M_x(CO)_y} PhNHCOH + PhNHCOOMe + PhNH_2 + PhNHCONHPh + PhN{=}NPh .$$

where M = Fe or Ru; the main products in the presence of ruthenium carbonyl are PhNHCOH and $PhNH_2$, while the products in the presence of iron cargonyl are PhNHCOOMe and PhNHCO. .NHPh.

The reduction of an aromatic nitro-compound in the presence of carbon monoxide and alcohol is of greater interest; carbamates, usually synthesised via a multistage process, are then obtained.[182] The ruthenium complexes $Ru_3(CO)_{12}$ and $Ru(CO)_3(PPh_3)_2$ are effective catalyst in the presence of tetraethylammonium chloride as the cocatalyst.[183] A monocarbamate has been obtained in 93% yield from the mononitro-compound, while the dinitro-compound gave rise to the dicarbamate in 50% yield:



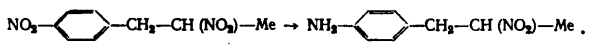
In the absence of the tetra-alkylammonium salt, the main product is aniline. The corresponding iron compounds are inactive. It has been suggested that the reaction proceeds via the formation of a nitrene derivative of ruthenium, i.e. $Ru_3(CO)_{10}NPh$. The same features have been observed when the reaction is carried out in the presence of the platinum complex $PtCl_2(PPh_3)_2$;[184] the reaction is promoted by Lewis acid.

5. Reduction by the CO + H_2O Mixture

The possibility of reducing nitro-compounds to the corresponding amines by the CO + H_2O mixture has been studied vigorously during the last ten years. Rhodium complexes are widely used. Rhodium carbonyl complexes $Rb_6(CO)_{16}$ and $[Rh(CO)_2Cl]_2$ catalyse the reduction of nitrobenzene at 150 °C and CO pressure of 50–120 atm; the yield of aniline reaches 85–95% and the formation of urea or formamide derivatives is not observed:[185]

$$PhNO_2 + 3CO + H_2O \rightarrow PhNH_2 + 3CO_2 .$$

Iron carbonyls are also active. The first stage is probably the formation of a nitrene derivative. If the reaction is carried out in pyridine[185] but in the presence of added *NN*-dimethylbenzylamine,[186] the selectivity is significantly higher. The attempt to heterogenise the catalyst by grafting it to the Amberlist A-2 resin modified with *NN*-dimethylbenzylamine was unsuccessful: the rate of hydrogenation fell and the senstivity of the catalyst to air increased. Aliphatic nitro-compounds are not reduced in this system, which made it possible to carry out a selective reduction:



The study of the role of amines[187] led to the conclusion that the acceleration of the reaction may be a consequence of the formation of a more active species incorporating the amine as a ligand. The $Rh_6(CO)_{16}$–γ-aminopyridine system, which makes it possible to reduce nitrobenzene under mild conditions (80 °C, CO pressure below 1 atm), is optimal. Other rhodium clusters are also active—$Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$; the iron and ruthenium clusters exhibit a low activity. It has been noted that the rate of reaction can be increased significantly in the presence of the $Rh_3(CO)_{12}$ and $Ru_3(CO)_{12}$ clusters only by introducing chelating nitrogen-containing bases into the reaction mixture.[188] Thus the yield of aniline reaches 100% after the introduction of 3,4,7,8-tetramethylphenanthroline or 3,4,5,6,7,8-hexamethylphenanthroline [189] in the proportions chelating agent : rhodium = 3.

The use of iron carbonyl $Fe(CO)_5$ as the catalyst of the reduction of nitrobenzene leads to the formation of aniline at 25 °C and a CO pressure of 50 atm if the reaction is performed in aqueous glyme with added triethylamine. Part of the catalyst is then irreversibly decomposed with formation of iron oxides.[190] The reaction proceeds rapidly at pH 12. The reducing species is $HFe(CO)_4^-$. $Rh_6(CO)_{16}$, $Os_3(CO)_{12}$, $H_2Os(CO)_{10}$, $H_4Os_4(CO)_{12}$, and $Ir_3(CO)_{12}$ are active under the same conditions. In their study of the reaction mechanism with the aid of CO + D_2O, the authors showed that, at least to the

extent of 88%, the reducing agent is the CO + D_2O mixture and not D_2 (reduction via the reaction CO + $D_2O \rightarrow CO_2 + D_2$), as suggested previously by Iqbal.[191] Furthermore, the rate of generation of deuterium (or hydrogen) is lower by two orders of magnitude than the rate of reduction of nitrobenzene, i.e. the reaction with molecular hydrogen does not play an important role.

At 80 °C and a CO pressure of 60 atm, the platinum complex $PtCl_2(PPh_3)_2$ is active in the presence of the Lewis acids $ZnCl_2$, $SnCl_2$, $SnCl_4$, etc., the highest rate being observed after the introduction of $SnCl_4$.[192] The yield of aniline falls on reducing the temperature or replacing the CO + H_2O mixture by hydrogen. The reaction takes place in stages, the Lewis acid being necessary in the second stage:[193]

$$PhNO_2 + 2CO \rightarrow PhN\langle + 2CO_2 ,$$

$$PhN\langle + CO \rightarrow PhNCO ,$$

$$PhNCO + H_2O \rightarrow [PhNHCOOH] \xrightarrow{-CO_2} PhNH_2 .$$

The dependence of the yield of aniline on the initial CO pressure has been noted for the ionic ruthenium complex $[Ru(COD)Py_4].(BPh_4)_2$. Thus the yield of aniline (in THF) is 36% at 15 atm, 62% at 30 atm, 74% at 45 atm, and 90% at 60 atm.[194] The authors rule out the possibility of the formation of an intermediate phenylnitrene derivative, since *o*-nitrobiphenyl produces only *o*-aminobiphenyl without an admixture of carbazole. The reaction does not occur when water is replaced by methanol or phenol.

The palladium complexes $Pd_3(CO)_3(PPh_3)_4$, $Pd_4(CO)_3(PPh_3)_4$, and $Pd_{10}(CO)_{12}(PPh_3)_6$, which are active and stable in the presence of an excess of triphenylphosphine, have been synthesised.[195]

In conclusion, we shall describe systems in which water may be replaced by unsaturated compounds. In the presence of $Rh_6(CO)_{16}$ the following reactions can be achieved with a high efficiency:[185]

$$2PhNO_2 + H_2 + 5CO \rightarrow PhNH{-}CO{-}NHPh + 4CO_2 \quad (70{-}80\%)$$

$$PhNO_2 + R{-}CH{=}CH_2 + 2CO \rightarrow Ph{-}N\langle_{CH_2{-}CH{-}R}^{CH_2} + 2CO_2 , \quad (60\%)$$

$$PhNO_2 + Ph{-}C{\equiv}C{-}Ph + 4CO \rightarrow Ph{-}N\langle_{C(=O){-}C(=O){-}Ph}^{C(=O){-}C{-}Ph} + 2CO_2 , \quad (85\%)$$

$$PhNO_2 + PhCHO + 3CO \rightarrow PhCH{=}N{-}Ph + 3CO_2 , \quad (60{-}85\%)$$

$$PhNO_2 + C_6H_4(CHO)_2 + 3CO \rightarrow C_6H_4(CH_2)(CO)N{-}Ph + 3CO_2 . \quad (50{-}60\%)$$

6. Reduction by Alcohols

A few studies are known where alcohols were used as reductants for aromatic nitro-compounds. Depending on the alcohol and the catalyst, the reaction products can be aromatic amines, 2,3-dialkylquinolines, hydrazo- and azo-derivatives, and arylhydroxylamines. When an aromatic nitro-compound reacts with an alcohol, hydrogen is transferred catalytically from the alcohol; aniline and an aldehyde (stage I) are then formed and can subsequently give rise to various condensation products (stage II). It has been shown that the ruthenium complex $RuCl_2(PPh_3)_3$ catalyses this reaction and a mixture of products is obtained:[196]

$$PhNO_2 + RCH_2CH_2OH \xrightarrow{180^\circ} PhNH_2 + \text{2-R-quinoline} + + PhNHCH_2CH_2R + PhN(CH_2CH_2R)_2$$

In methanol and isopropyl alcohol, the reaction proceeds selectively (stage I alone); in ethanol, propanol, and butanol, it is possible to obtain 10–40% of quinolines (stage II). A reaction scheme has been proposed to which a ruthenium chelate complex of a Schiff base dimer is an intermediate.[197] A high yield of mono- and di-alkylquinolines is attained in the presence of equimolar mixtures of rhodium and molybdenum complexes;[198] the latter complex, as a Lewis acid, promotes the condensation reaction.

In the absence of molybdenum compounds, rhodium complexes catalyse only the first stage.[199]

Rhodium complexes containing triphenylphosphine are active in solution in a base. Under these conditions, dinitro-compounds are not reduced.[198] The iridium complexes $Ir^I(X)(CH_2{=}CH_2)_2Cl$, where X = 2,2-bipyridyl or 1,10-phenanthroline and some of its derivatives, is the most active.[200] The activity is satisfactorily correlated with the pK_a of the chelate [chelating agent?]. The reduction reaction proceeds in stages and, by altering the alkali : catalyst ratio, it is possible to obtain a high yield of azo- or hydrazo-derivatives. In the presence of the 4,4-diphenylbipyridyl complex, arylhydroxylamine was isolated in a high yield.

The above procedure is extremely promising, permitting the simultaneous synthesis of products of practical importance (for example, anilines and ketones or aldehydes). Extensive search for more active, stable, and readily available catalysts is essential.

IV. ENZYMIC REACTION OF AROMATIC NITRO-COMPOUNDS

The biological activity of aromatic nitro-compounds, which is manifested by their toxicity[201] (cardiac poisons) and mutagenic,[202] carcinogenic,[203–205] and antibacterial[206–209] activities, is associated with their enzymic reduction. The reduction to aromatic amines or other derivatives is effected by animal tissue homogenates (animals ranging from fish to mammals[210,211]) under aerobic conditions. In animal organisms, aromatic nitro-compounds accumulate mainly in the liver, so that most of the studies have been devoted to the metabolism of aromatic nitro-compounds in mammalian livers.

It has been shown that the reducing activity is localised both in the soluble (cytosol) fraction and in the microsomal fractions, the electron donors being NADP and NADP-H_2 (nicotinamide adenine dinucleotide phosphate and its reduced form). The reduction in cytosol is catalysed by xanthine oxidase[212–214] or DT-diaphorase[215] (enzymes containing an iron–molybdenum cluster linked to sulphur[216,217]). In the microsomal fraction, the reduction of aromatic nitro-compounds is catalysed by other enzymes. *p*-Nitrobenzoic acid can be reduced by purified NADP-H_2-cytochrome *c* reductase, isolated from microsomes, in the presence of flavin adenine dinucleotide.[213,218] Cytochrome P-450 [219–220] or cytochrome b_5 in the presence of NADP-cytochrome b_5 reductase also possess reducing capacity. Later studies established that both microsomal components—NADP-H_2-cytochrome P-450 reductase and cytochrome P-450—are essential for the reduction of nitrobenzene to aniline.[222] The reductase catalyses the first stage in the reduction of the nitro-group, while both components are essential for the reduction of the intermediate arylhydroxylamine. The same features have been observed also in the reduction of *p*-nitrobenzoic acid. The authors note that nitrobenzene-reducing activity is in the main concentrated in the microsomal fraction, while the cytosol fraction exhibits a low activity.

The high activity of an enzyme system comprising three protein components, namely cytochrome b_5, NADP-cytochrome b_5 reductase, and an unknown protein factor, has been noted.[221] The necessity for the presence of several enzymes has also been emphasised in other studies.[223–225] It a study involving microsomal enzymes from

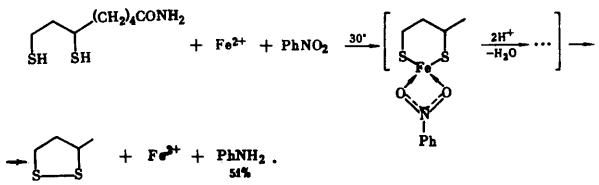
mouse liver homogenate, it has been shown that there are at least two uridine diphosphate transglucuronylases, in the presence of which it is possible to synthesise glucuronide from uridine diphosphate glucuronate and *p*-nitrophenol.[223-225]

The final products of the reduction of aromatic nitro-compounds are usually the corresponding anilines, but it is possible to isolate also intermediate reduction products. It has been shown[203] that the reaction proceeds via the pathway $-NO_2 \rightarrow -NHOH \rightarrow -NH_2$, different enzymes being active in the first and second stages.

The reduction of 2,4-dinitrotoluene (by cytosol xanthine oxidase) to 2,4-diaminotoluene takes place in stages via 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene.[226,227] Nitroso-derivatives have not been observed, although their formation is entirely probable, since it has been shown that nitrite reductase in micro-organisms and plants reduces nitrite to hyponitrite and further to hydroxylamine and ammonia:

$$NO_2^- \rightarrow N_2O_4^{2-} \rightarrow NH_2OH \rightarrow NH_3 .$$

The enzymes are known to contain iron thiols;[217] studies[228,229] on the reduction of monosubstituted nitrobenzenes in the presence of the dihydrolipoamide (coenzyme in acyl transfer and redox reactions)—iron(II) system in a weakly basic medium are therefore of interest:



It has been noted that the system is unreactive in relation to the reduction of C=C, C=O, CN, and ester groups. The yields of the products (in %) are as follows:

(a) for *p*-substituted aromatic nitro-compounds:

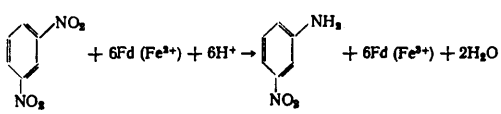
CH_3	OCH_3	NH_2	CN	$COCH_3$	$OCOCH_3$	Cl
35	73	77	94	90	66	58

(b) for *o*-substituted aromatic nitro-compounds:

$COCH_3$	CHO	OCH_3	NH_2	CN
73	67	81	97	84

In the series of thiols, the highest activity is shown by cysteine.

The reduction of 2,4-dinitrophenol, nitrobenzene and *m*-dinitrobenzene by ferredoxin (and iron-containing protein) has been described:[230]

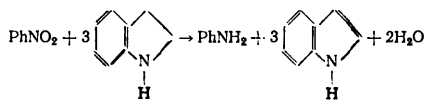


where $Fd(Fe^{2+})$ is the reduced form of ferredoxin, which acts in this reaction as a single electron donor. 2,4-Dinitrophenol is reduced under these conditions to 2-amino-4-nitrophenol.

It is seen from the data presented in this Section that the enzymic reduction of aromatic nitro-compounds takes place in the same way as the reduction by transition metal complexes. An unusual feature is that the enzyme systems are mainly iron and molybdenum clusters linked to sulphur. Comparison of the enzyme systems with coordination compounds shows that the enzyme systems are more selective and that catalytic properties most similar to theirs are shown by platinum group metal complexes with highly conjugated ligands.[4]

V. OTHER REACTIONS

Hydrogen transfer from cyclic amines to aromatic nitro-compounds catalysed by noble metal salts has been described:[231,232]



A high activity has been observed for $RuCl_3.H_2O$ and $RhCl_3.3H_2O$, in the presence of which the yield of aniline is 88 and 82% respectively. Palladium, rhenium, and platinum chlorides are weakly active, while cobalt and nickel compounds and phosphine complexes of rhodium and ruthenium do not catalyst the reaction. Secondary cyclic amines—indoline, tetrahydroquinoline, 3-pyrroline, piperidine, and pyrrolidine—are effective hydrogen donors. The authors explained this by their pronounced coordinating properties. The rate-limiting stage is the activation of the nitro-group, since the intermediate nitrosobenzene and phenylhydroxylamine are reduced under these conditions faster by two orders of magnitude than the nitro-group, while azo- and hydrazo-benzene are reduced an order of magnitude faster. A mechanism involving the coordination of the aromatic nitro-compound to the complex has been suggested:

$$RhCl_3 + Ind \rightarrow Rh^ICl + Inl + 2HCl ,$$
$$Rh^ICl + PhNO_2 \rightarrow Rh^ICl(PhNO_2) ,$$
$$Rh^ICl(PhNO_2) + 3Ind \rightarrow Rh^ICl + PhNH_2 + 3Inl + 2H_2O .$$

where Ind = indoline and Inl = indole.

The direct synthesis of the anilides RCONHPh from an aromatic nitro-compound and organic acids RCOOH can be achieved by employing molybdenum carbonyl.[233] Depending on the substituent, the yield of anilides ranges from 46 to 85%. The reaction is selective with respect to the nitro-group; the C=C bond and the OH, C=O, OCH_3, COOH, NH_2, CN, etc. groups are not reduced. In the presence of another catalyst, namely $RuCl_2(PPh_3)_3$, and added triethylamine, aniline was obtained under the same conditions.[234] The $PtCl_2(PPh_3)_2 + SnCl_2$ system exhibits activity in the reductive acylation of aromatic nitro-compounds in a CO atmosphere:[235]

$$PhNO_2 + RCOOH + 3CO \rightarrow PhNHCOR + 3CO_2 .$$

$SnCl_4$ can be replaced here by other Lewis acids.

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Thus one may conclude that the use of coordination compounds in the chemistry of aromatic nitro-compounds is developing vigorously; this has made it possible to obtain complexes with a fundamentally new structure and complex catalysts effective and selective in reduction reactions can be created on the basis of theoretical ideas. It is likely that coordination compounds based on aromatic nitro-compounds may possess interesting biological properties (see, for example, Nishida et al.[236]).

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The Structure and Electron-donor Properties of Organic Compounds of Selenium(II)

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The results of studies of the structure and complex-forming power of organic compounds of selenium have been summarised. The principal characteristics of the geometry of the molecules and their orbital state and electron-donor properties have been discussed. Quantitative estimates of the complex-forming power of selenium compounds have been given. The questions of the generation of selenium-centred free radicals and their stabilisation by complex formation have been examined. The bibliography contains 225 references.

CONTENTS

I. Introduction 433
II. Selenides 433
III. Compounds of the type $R_nE=Se$ 438
IV. Diselenides 440
V. Selenium-containing free radicals 442

I. INTRODUCTION

The organic chemistry of selenium has developed intensively in recent years, and is acquiring increasing importance in various branches of science and technology. One factor responsible for this was the discovery of the part played by selenium in living organisms.[1-3] The biochemical role of this element was understood when it was shown that selenium-containing proteins are components of various enzymes.[3] Another important factor in the development of the organic chemistry of selenium was the discovery of "organic metals", that is organic superconductors obtained from charge-transfer complexes and radical-ion salts using selenium compounds.[4,5] Research is being carried out to find new promising selenium-containing compounds for these purposes, and their structures are being studied.[6-9] Organic selenium compounds are used to obtain films of semiconducting materials.[10] In addition, a number of organoselenium compounds are highly reactive towards free radicals, and this opens up the possibility of their use as antioxidants.[3] There are indications that selenium compounds are more effective antioxidants than the corresponding sulphur compounds.

Various aspects of the chemistry of selenium have been dealt with in a monograph,[1] collected papers,[2,3] and reviews,[11-13] but a number of problems which have developed in recent years have not yet been summarised. This applies, in particular, to studies of the electronic structure and orbital state of organoselenium compounds, and their complex-forming power.

An extremely important aspect of the electronic structure of molecules is the nature of the occupied and unoccupied molecular orbitals: their energy, symmetry, and degree of delocalisation. Of particular interest are the boundary orbitals—the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals, since the nature of these orbitals is the main factor determining such important properties of molecules as the ionisation potential, electron affinity, spectral properties, and reactivity, including complex-forming power. Published summaries of the coordination properties of selenium compounds deal chiefly with inorganic compounds[11] and complexes with transition metal ions.[12,13]

In the present review, an attempt has been made to summarise the results, obtained chiefly in recent years, of studies of the geometry and molecular-orbital state of organic compounds of divalent selenium, and their coordination properties with respect to acceptors of different types (σ, ν, π). Particular attention has been paid to the quantitative estimation of the electron-donor power of organoselenium compounds. The questions of the generation of selenium-containing free radicals and their stabilisation by complex formation have been examined.

II. SELENIDES

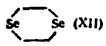
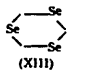
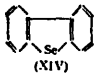
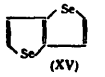
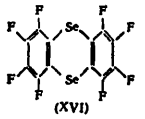
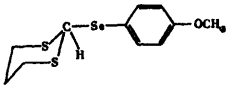
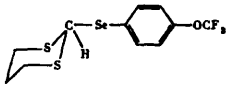
1. The Geometry and Molecular-Orbital State of Selenides

The selenium atom in organic selenides R_2Se, as in compounds of the type RSe−SeR or $R_nE=Se$ (E = C, P) in accordance with the state of the valence electrons $4s^2p_z^2p_xp_y$, has two bonded (p_x, p_y and four non-bonded (s^2, p_z^2) electrons. The extent of the participation of the atomic orbitals of selenium in the formation of the molecular orbitals of a given compound to a large extent determines the geometry of the molecules and their properties.

The structural parameters of a number of selenides, found by X-ray diffraction (XRD) in the crystalline state, by microwave spectroscopy (MWS) and by electron diffraction (ED) in the vapour are given in Table 1. For a complete picture, Table 1, in addition to data obtained in recent years, also includes data given earlier.[2,3] Judging from the values of the valence angle CSeC (92−96°) for the aliphatic selenides (I)−(V), the participation of the valence 4*s* orbital in the formation of the Se−C σ-bond in these compounds is slight. In the aromatic compounds (VI)−(VIII), the CSeC angle is larger, 100−106°. The Se−C bond lengths depend to a marked extent on the state of hybridisation of the carbon atom, and have the following values: for the aliphatic compounds (Se−C_{sp^3}) 1.94−1.98 Å (I)−(V), (XVII), (XVIII), for the aromatic compounds (Se−C_{sp^2}) 1.90−1.92 Å (VI)−(X), (XVII), (XVIII), and for Se−C_{sp} (selenocyanate group) 1.84−1.85 Å (IV), (IX). The differences in the Se−C bond lengths for aliphatic and aromatic compounds can be seen particularly clearly by comparing the data for the cyclic compounds(XII), (XIII), and (XIV)−(XVI). The observed changes in the bond length in the order Se−C_{sp^3} > Se−C_{sp^2} > Se−C_{sp} are fairly large, and apparently cannot be attributed entirely to the differences in the state of hybridisation and hence in the dimensions of the corresponding carbon atoms. Thus the difference in the C−H bond lengths for different valence states of the carbon atom does not exceed 0.03 Å: C_{sp^3}−H (1.09), C_{sp^2}−H (1.07), C_{sp}−H (1.06 Å), whereas in the CC multiple bond series, these differences

are ten times greater: $C_{sp^3}-C_{sp^3}$ (1.54), $C_{sp^2}-C_{sp^2}$ (1.39), $C_{sp}-C_{sp}$ (1.20 Å). Comparison of these data makes it possible to regard the decrease in the length of the Se–C bond in the above series as evidence of additional Se–C bonding as a result of the interaction of the lone pair of electrons (LPE) of the selenium atom with the π-system of the electrons of the aromatic (unsaturated) fragment ($p\pi$-conjugation).

Table 1. Structural parameters of selenides.

Selenide	Bond length, Å		Angle CSeC, °	Method	Refs.
	$Se-C_{sp^3}$	$Se-C_{sp^2}$			
CH_3SeH (I)	1.959	—	95.5	MWS	[14]
CH_3SeCH_3 (II)	1.943	—	96.2	MWS	[15]
CF_3SeCF_3 (III)	1.978	—	95.5	ED	[16]
CF_3SeCN (IV)	1.984	*	92.2	ED	[17]
$(C_6H_5COCH_2)_2Se$ (V)	1.951	—	96.3	XRD	[18]
$C_6H_5SeCH_3$ (VI)	1.957	1.912	99.6±2.5	ED	[19]
C_6H_5SeBr (VII)	—	1.899	99.8±1.2	ED	[20]
$(4\text{-}CH_3C_6H_4)_2Se$ (VIII)	—	1.925	106.2	XRD	[21]
$1,4\text{-}C_6H_4(SeCN)_2$ (IX)	**	1.916	94.4±0.9	XRD	[22]
$2\text{-}NO_2C_6H_4SeBr$ (X)	—	1.917	98.5	ED	[23]
$2\text{-}CHOC_6H_4SeBr$ (XI)	—	1.876	98.0	XRD	[24]
 (XII)	1.99; 2.04	—	98±3.5	XRD	[25]
 (XIII)	1.945; 1.947; 1.967	—	96.8±1.0; 100.3±1.0	XRD	[26]
 (XIV)	—	1.899	86.6±0.2	XRD	[27]
 (XV)	—	1.87	86.0±1.0	XRD	[28]
 (XVI)	—	1.87—1.90	96.2—97	XRD	[29]
	1.966	1.915	100.8	XRD	[30]
	1.963	1.920	100.6	XRD	[30]

*Se–CN bond length 1.854 Å, **1.837 Å.

A similar sequence is observed in the change in the dipole moments of the Se–C bonds. The dipole moments of the Se–C bonds,[31] calculated from the experimental dipole moments of the corresponding compounds by the vector additivity method, are:

$$\overleftarrow{Se}-C_{sp^3}\ 0.70 > \overleftarrow{Se}-C_{sp^3\,(unsaturated)}$$

$$0.53 > \overleftarrow{Se}-C_{sp^3\,(aromatic)}\ 0.30 > \overleftarrow{Se}-C_{sp}\ -0.75\ (Д).$$

The decrease in the dipole moment of the Se–C bond for different valence states of the carbon atom, and the change in its direction (for $Se-C_{sp}$) may be due to a number of factors. In Ref.31, the observed changes in the dipole moments were attributed to differences in the electronegativity of the carbon atom in different valence states:

$$C_{sp^3}\text{—}2.6,\ C_{sp^3\,(unsaturated)}\ \text{—}2.7,\ C_{sp^2}\ \text{—}2.8,\ C_{sp}\ \text{—}3.2,$$

electronegativity of the selenium atom –2.4.[32] The sequence indicated, however, may be determined not only by this factor but also by the changes in the lengths of the corresponding bonds, and also by the possibility of charge transfer from the selenium atom to the aromatic (unsaturated) p-electron system ($p\pi$-conjugation).

The idea of possible $p\pi$-conjugation in aromatic and unsaturated selenium compounds is often used to explain the properties of the corresponding compounds, as described below. The most reliable information on the orbital state of molecules is given by photoelectron spectroscopy (PES). When combined with quantum-chemical calculations in the approximation of Koopman's theory, according to which the ionisation potential is equal to the energy of the corresponding orbital with the sign reversed ($IP_i = -\varepsilon i$), this method makes possible the quantitative characterisation of the orbital state of molecules.

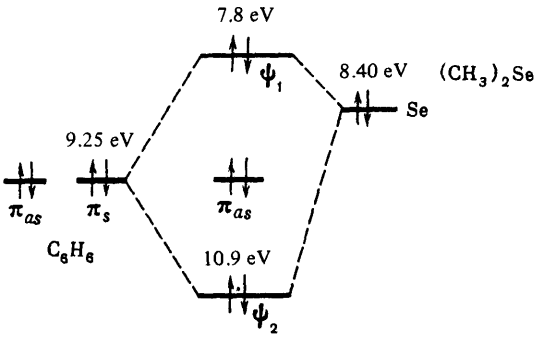


Figure 1. Formation of the HOMO of selenoanisole.[35]

According to quantum-chemical calculations, the first ionisation potential of aliphatic selenides corresponds to an HOMO which is a 4p orbital populated chiefly by an LPE of the selenium atom.[33] An interesting feature is that this orbital is the HOMO not only in dialkyl selenides but also in the series of compounds $(H_3M)_2Se$, where M = Si, Ge.[34] The HOMO of the aromatic selenides includes not only a 4p orbital of the selenium atom but also a contribution from the π_s orbital of the aromatic fragment. The formation of the molecular orbitals of selenoanisole is represented in Fig.1.[35] The mixing of the π_s orbital of the aromatic fragment with the p orbital of the LPE of the heteroatom raises the HOMO relative to the levels of the orbitals of the interacting fragments. Estimation of the contribution of the LPE of the selenium atom to the HOMO of selenoanisole by the HMO method with the parametrisation of the PES calculation[36–38] gave the value 0.834,[39] which is appreciably greater than that for the anisole molecule (0.446) and close to the contribution for the thioanisole molecule (0.738). According to Ref.40, the contribution of the LPE of the heteroatom to the HOMO of the compounds $C_6H_5ECH_3$ of the oxygen sub-group increases in the order: O (0.54) < S (0.77) < Se (0.84) < Te (0.89). The opposite order was obtained in an estimation of the contribution of the π-component of the aromatic fragment.[41] Similar results were obtained by calculating the resonance integrals $\beta(C_{sp^2}-E)$,

where E = O, S, Se, for compounds $C_6H_5ECH_3$. The participation of the LPE of the selenium atom in the general $p\pi$-conjugation system is indicated by the results of the determination of the dipole moments of the interaction ($\Delta\mu_{int}$) for substituted selenoanisoles[42] and phenylselenoacetylenes.[43]

The state of the HOMO is extremely sensitive to the steric and electronic effects of the substituents. For *p*-substituted selenoanisoles, a linear relationship has been established between the first ionisation potential (IP_1), characterising the energy of the HOMO, and the σ^+-constants of the substituents.[39] A similar relationship between IP_1 and σ_m was established for disubstituted selenophenes.[44] For the aromatic compounds C_6H_5SeR, the conformation of the selenide molecules, like that of the corresponding compounds of oxygen and sulphur, is determined to a large extent by the competition between two effects: $p\pi$-conjugation (which is a maximum for a planar molecule, when the angle φ between the plane of the phenyl ring and the CSeC plane is 0°) and steric effects (the tendence for the SeR group to be displaced from the plane of the ring as a result of the mutual repulsion of the substituent R and the *ortho*-hydrogen atoms of the phenyl ring). Depending on the contributions of these effects, which determine the barrier to the rotation of the SeR group relative to the aromatic fragment, an affective conformation of the molecule with a definite angle φ, or an equilibrium between planar (φ = 0°) and orthogonal (φ = 90°) conformers can apparently be produced.

From the doublet character of the first PES band of selenoanisole, it was concluded that the gas phase contains two rotamers;[3] the first component of the band (8.0 eV) was assigned to the HOMO of a planar conformer, and the second (8.3 eV) to a rotamer with minimum overlap of the $4p-\pi$-orbitals. Judging from the intensity of these bands, the ratio of the rotamers is ~1 : 1. At the same time, PES did not detect the presence of rotamers for the corresponding compounds C_6H_5SeR (R = C_2H_5 or iso-C_3H_7) where the 8.3 eV band was assigned to an orthogonal conformer.[45] The differences in the energies of the rotamers are small, even for the corresponding oxygen and sulphur compounds. Thus the difference between the energies of the planar and orthogonal conformers does not exceed 1.3 kcal mole^{-1} for anisole ,[46] and 0.8 kcal mole^{-1} for thioanisole.[47,48] For the selenium compounds, the difference between the energies of the planar and orthogonal conformations should be even smaller. This is apparently one of the reasons why they cannot be distinguished by some methods. Studies of the dipole moments and Kerr constants of selenoanisole and diphenyl selenide in inert solvents indicated that these compounds are conformationally homogeneous, with an angle φ = 32° for the first compound[49] and φ = 48° for the second.[50] According to electron diffraction data, the angle φ in the selenoanisole molecule in the gas phase is 40 ± 13°.[19] The introduction of electron-acceptor substituents in position 4 of the phenyl ring of selenoanisole leads to flattening of the molecules: for the 4-Cl- and 4-Br-derivatives, $\varphi < 20°$, and for the 4-NO_2-derivative, $\varphi \simeq 0°$.[49] At the same time, the ^1H and ^2H NMR spectra of 4-chloroselenoanisole in a liquid-crystal solvent[51] indicated that the angle of rotation of the phenyl ring relative to the CSeC plane is ~40°. The planar *s-trans*-structure with a maximum conjugation is characteristic of aryl vinyl selenides.[52] According to the dipole moments and the Kerr constants, the C_6H_5SeCN molecule, unlike selenoanisole, has a planar conformation.[53] The infrared (IR) spectra of crystalline specimens in polarised light[54] also detected no signs of conformational non-homogeneity in aryl selenocyanates. Electron-donor substituents (OCH_3, $N(CH_3)_2$ in position 4 of the phenyl ring do not break down the planar conformation of phenyl selenocyanates, but electron-acceptor substituents (Cl, Br, NO_2) lead to slight breakdown of the coplanarity of the C_6H_4SeCN fragment.[53] Birefringence established an increase in the non-coplanarity of 1,4-disubstituted compounds of selenium of the type $RSeC_6H_4SeR$ (R = CN or CH_3), compared with the monosubstituted compounds.[55] In a study of the conformation of the molecules of aliphatic selenides R_2Se (R = CH_3, C_2H_5), proton magnetic resonance data, in agreement with IR and Raman spectroscopic data, showed that in these compounds there is free rotation of R about the C–Se bond.[56] The IR and Raman spectra of diethyl selenide in argon and nitrogen matrices, however, indicate the existence of conformational isomerism in the solid state.[57] NMR is extremely promising for the study of the electronic and geometric structure of organic selenides. Various nuclei are studied, including the ^{77}Se isotope, whose natural concentration is 7.6%.

The differences between the chemical shifts δ of ^{77}Se in different compounds are fairly large (in a number of cases reaching 10^2-10^3 p.p.m.[58,59]) and are not sensitive to the solvent,[59,60] and this makes possible a fairly reliable determination of the electronic state of the molecules.

The number of published papers on the study of organic selenides by ^{77}Se NMR has increased considerably in recent years, Since the chemical shift reflects the charge state of an atom, the values of δ for ^{77}Se are sidely used in studies of intramolecular electronic interactions. For a large group of compounds of the type XC_6H_4SeR, a linear relationship has been established between δ for ^{77}Se and the Hammett constant σ (X).[59] A more detailed ^{13}C and ^{77}Se NMR study of compounds of the type XC_6H_4SeR indicated that δ $^{13}C(1)$ are linearly correlated with σ_I and σ_R of the substituents.[61] The values of δ ^1H, δ ^{13}C, and δ ^{77}Se have been used in studies of the conformation and intramolecular electronic interactions in a number of compounds: $PhSeCH=CH_2$,[62] $CH_3SeC\equiv CR$,[63] mono-, di-, and triseleno-substituted ethylenes,[64] and condensed five-membered heterocyclic compounds based on selenophene.[65] Data on the temperature dependence of δ ^{77}Se for phenylselenylcyclohexane derivatives have been used to estimate the barrier to inversion of the cyclohexyl fragment.[66] ^{77}Se NMR has been used to study the structure of molecules containing selenium–sulphur bonds, of the type XC_6H_4Se-SR, which provide models of biological systems.[67] Measurements of the ^{77}Se and ^{125}Te chemical shifts for analogous organic selenides and tellurides indicated that there is a linear relationship between these quantities: δ Te = 1.60 δ Se.[68,69] The relationship between δ ^1H, δ ^{13}C, and δ ^{77}Se for cyclic compounds of selenium has been studied.[70,71] ^{77}Se NMR gives extensive information on the composition of the compounds formed in the binary sulphur–selenium system.[72]

In addition to the chemical shift of the selenium atom, another parameter extremely sensitive to change in the electronic structure of molecules is the spin–spin coupling constant $^1J(^{77}Se-^{13}C)$. In a series of selenides RSeR', this constant increases with increase in the *s*-character of the hybridised orbital or the carbon atom forming the bond with the selenium atom.[73,74] In a series of selenoanisoles, $^1J(^{77}Se-^{13}C)$ increases when acceptor substituents (4-NO_2-) are introduced into the aromatic ring, and decreases when donor substituents (4-NH_2-) are introduced, due to the change in the intensity of the $p\pi$-conjugation and the Se–C bond order.[73] In Ref.75, the stereochemistry of aromatic compounds of selenium was studied using the spin–spin coupling constant of atoms at a greater distance from one another, namely $^2J[^{77}Se-^{13}C(2, 6)]$. The nature of the dependence of $^2J[^{77}Se-^{13}C(1)]$ on the number and nature of the *ortho*-substituents in various aromatic compounds of selenium has been established. The influence of the $^{13}C:^{12}C$ isotope effect on the shielding of ^{77}Se in compounds RSeR' has been determined,[76] and a correlation between Δ ^{77}Se and the length of the Se–C bonds established. The measured spin–spin coupling constants of the selenium nuclei for a number of dialkyl polyselenides $R-(Se)_n-R$ (n = 2–5) indicated that the polyselenide chain has a linear structure.[77]

Valuable information on the electronic and spatial structure of aromatic and unsaturated compounds of selenium is provided by ^{13}C NMR. For selenides C_6H_5SeR, the values of δ for ^{13}C in position 4 of the phenyl ring (relative to TMS) are as follows:[78]

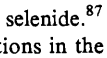
R	CH_3	C_2H_5	C_3H_7	*iso*-C_3H_7	$C(CH_3)_3$
$\delta^{13}C$ (4)	125.55	126.24	126.16	126.84	128.10

The differences in the inductive constants of these R are comparatively small, so that they should have practically no influence on the charge state and hence on the magnitude of δ for the C(4) atom. The observed nature of the change in δ $^{13}C(4)$ with increase in the size of R reflects the influence of steric effects on $p\pi$-conjugation in aromatic selenides; this is indicated by the fairly good correlation between $\delta^{13}C(4)$ and the steric constants E_s^0 of the substituents.[78] ^{13}C NMR has been used to determine the dependence of the degree of $p\pi$-conjugation and the conformational state on the nature of the substituents in substituted selenoanisoles.[79–81] Acceptor substituents lead to an improvement, and donor substituents to a deterioration, in the conditions for $p\pi$-conjugation and hence for coplanarity of the molecules. The relationship between the values of σ for ^{13}C and the constants σ_I and σ_R of the substituents has been established for phenyl vinyl selenides[82] and divinyl selenides.[83] δ ^{13}C data have been used to determine the previously unknown values of σ_R^0 for the selenium-containing substituents C_2H_5Se (–0.12) and $CH_2=CHSe$ (–0.09),[83] and ^{19}F NMR data for the *para*-fluorine atom in the aromatic fragment have been used to determine σ_p for the substituents CF_3Se (0.44) and $(CF_3)_3CSe$ (0.54).[84] The interaction of the LPE of the selenium atom with the π-electron system of the aromatic (unsaturated) fragment has been studied by ultraviolet spectroscopy combined with quantum-chemical calculations. The nature of the electron transitions has been studied in derivatives of selenoanisole and their isologues[85] and in substituted aryl allyl selenides,[86] alkyl vinyl selenides, and divinyl selenide.[87] Quantum-chemical calculations of the electron transitions in the PPP approximation have shown that the resonance integrals and hence the degree of $p\pi$-conjugation in a series of analogous compounds of the group VI elements decrease in the order: $\beta(C-O) \gg \beta(C-S) > \beta(C-Se) > \beta(C-Te)$.[85,87] Possible $p\pi$-bonding in the compounds $CH_2=CH-C\equiv CSeCH_3$ and $C_2H_5C\equiv C-C\equiv CSeCH_3$ is indicated by the results of quantum-chemical calculations (CNDO/2).[88] At the same time, studies of the IR spectra of selenoanisole, phenyl selenocyanate, and their derivatives[89,90] showed that the spectra of these compounds represent the sum of the practically non-perturbed spectra of the phenyl ring and the $SeCH_3$(SeCN) group), from which it was concluded that there is very little intramolecular interaction. As the authors themselves point out, however, this conclusion was reached without carrying out a normal-coordinate analysis, so that it is not sufficiently well-founded.

2. The Electron-Donor Properties of Selenides

The properties of selenides as electron donors is determined to a large extent by the state of the HOMO, and primarily by its energy and symmetry. According to quantum-chemical calculations (CNDO/2) for dimethyl selenide, the contribution of the LPE of the selenium atom to the HOMO is 0.88, so that the charge on the selenium atom is 0.77.[88] Evidence that the HOMO of aliphatic selenides consists chiefly of the $4p^2$-LPE of the selenium atom is provided by the results of structural studies of the complexes formed by selenides. Table 2 gives the published structural parameters of complexes of selenides with σ-acceptors (A = I_2, ICl) and ν-acceptors (A = $PdCl_2$, $PtBr_2$). The angle (<C–Se–A) formed by the coordinate bond Se–A with the Se–C bond is 100–107°, that is the donor–acceptor bond Se–A, in accordance with the orientation of the orbital of the $4p^2$-LPE, is almost perpendicular to the plane of the C–Se–C bonds of the selenide molecule. The lengths of the intermolecular bonds (r_{DA}) of the complexes vary over a fairly wide range; this can be clearly seen by comparing the values of $\Delta r = e_{DA}^{expt} - (r_D + r_A)_{cov}$, where r_{DA}^{expt} is the experimental length of the intermolecular bond, and r_D and r_A the covalent radii of the atoms of the molecules of the donor and the acceptor involved in the formation of the donor–acceptor bond (the covalent radii of the atoms given by Pauling[98] were used in the calculations). For the comparatively weak complexes formed by selenides with halogens, the values of Δr are large, whereas for the complexes with compounds of Pd and Pt, the length of the intermolecular bond is practically equal to the sum of the covalent radii of the corresponding atoms.

Table 2. Structure of selenide complexes.

Complex	D–A bond	r_{DA}, Å	Δr*, Å	C–Se–A angle, °	Refs.
	Se–I	2.762	0.26	100.5	[91]
	Se–I	2.829	0.33	100.5	[92]
	Se–I	2.755	0.25	107.0; 102.0	[93, 94]
	Se–I	2.630	0.13	104.1; 99.0	[93]
$PdCl_2 \cdot 2(C_4H_9)_2Se$	Se–Pd	2.424	0	100.8; 109.5	[95]
$PdCl_2 \cdot [CH_3SeCH(CH_3)_2]_2$	Se–Pd	2.40 2.36	–0.07	105.5; 103.7; 107.4; 104.2	[96]
$PtBr_2 \cdot 2$ 	Se–Pt	2.43	0	110.5; 107.2	[97]

*$\Delta r = r_{DA}^{expt} - (r_D + r_A)_{cov}$.

From the previously established relationship between $-\Delta H$ and Δr,[99] covering a wide range of molecular complexes of the $n\nu$ and $n\sigma$ types, including the complexes of selenides with a number of acceptors, the energy of formation of the Pd–Se and Pt–Se bonds in these complexes should be greater than 15 kcal mole^{-1}.

Complex formation by organic selenides with iodine has been studied in most detail by electronic spectroscopy.[100–134] The spectra of the complexes contain new bands, charge-transfer bands (CTB), not present in the spectra of the starting materials. The positions (ν_{CTB}) and energies ($h\nu_{CTB}$) of the charge-transfer bands in the spectra of the complexes have been established, and the stability constants determined. The temperature dependence of the equilibrium constants has been used to determine the thermodynamic parameters of complex formation by iodine with alicyclic[101] and cyclic selenides,[102,103] and with aromatic selenides of the substituted selenoanisole[104–109] and diphenyl selenide[100,110,111] types. In Ref.112, complex formation by selenides of different kinds with iodine was studied not only by electronic spectroscopy but also by calorimetric titration. The compositions and enthalpies of formation of the complexes were determined, and their electronic spectra studied. The values of $-\Delta H$ for the complexes of a number of selenides with iodine are given in Table 3. For aliphatic selenides, equations were obtained, relating the values of $-\Delta H$ to $h\nu_{CTB}$ and $-\Delta H$ to $\Sigma\sigma^+$ (the sum of the inductive constants of the substituents). Aromatic selenides, like the aliphatic compounds, behave as

n-donors towards I_2, and the coordination centre is the selenium atom. A noteworthy feature is that the absolute values of $-\Delta H$ for the complexes of I_2 with aromatic selenides are smaller than those for aliphatic selenides (Table 3); this is apparently related not only to the differences in the influence of the inductive effects but also to the expenditure of energy to break down the $p\pi$-conjugation in the aromatic selenides. According to Raman spectroscopic data, the wavenumber of the I—I vibrations decreases from 215 cm^{-1} in the original I_2 molecule to 165 cm^{-1} in the complex $(CH_3)_2Se.I_2$ and 160 cm^{-1} in the complex $(C_2H_5)_2Se.I_2$.[113] The stretching wavenumber of the intermolecular Se—I bond in the complex $(C_2H_5)_2Se.I_2$ was found to be 100 cm^{-1}.[114] This value is much lower than the vibrational wavenumber of the intermolecular Se—B bond (256 cm^{-1}) in the complex $(CH_3)_2.Se.BF_3$.[115] These differences are apparently due to the difference in the strengths of the intermolecular bonds in these complexes. Systematic spectral studies of complexes of iodine with substituted selenoanisoles[104–109] revealed a number of general regularities of complex formation. A linear relationship was established between the values of $-\Delta H$ and the constants $\sigma_{m,p}$ of the substituents in the phenyl ring, and also between $-\Delta H$ and the displacement of the iodine band in the electronic spectrum on complex formation $\Delta\nu_{I_2}$, and between the changes in the enthalpy ΔH and the entropy ΔS in complex formation.[104–106] The solvatochromism of the charge transfer bands was used to study the influence of solvents of different character on the thermodynamics of the formation of complexes of selenoanisoles with iodine.[108,109] Analysis of the experimental data showed that the observed differences in the values of $-\Delta H$ for a given complex in different solvents are due chiefly to the contribution of the specific solvation of the iodine molecule. For the molecules of the donor and the complex in the series of solvents studied, specific solvation takes place for the most part.

Table 3. Enthalpies of formation of the complexes (kcal $mole^{-1}$).

Selenide	I_2 (Ref.112) 1:1	$AlBr_3$ (Ref.129) 1:1	$SnCl_4$ (Ref.128) 1:1	$SnCl_4$ (Ref.128) 1:2
$(C_2H_5)_2Se$	9.9	—	—	—
$(C_3H_7)_2Se$	9.7	29.9	14.3	27.7
$(C_4H_9)_2Se$	10.2	—	14.6	28.4
$(C_8H_{17})_2Se$	9.8	30.1	13.9	27.8
$(C_6H_5CH_2)_2Se$	9.2	27.4	—	—
$C_6H_5SeCH_3$	7.6	24.9	—	—
$C_6H_5SeC_3H_7$	8.4	26.2	—	—
$C_6H_5SeCH_2CH{=}CH_2$	8.0	26.1	—	—
$(C_6H_5)_2Se$	3.6	22.6	—	—
$(4\text{-}CH_3C_6H_4)_2Se$	—	23.8	—	—

Organic selenides form complexes with π-acceptors; the complexes of aromatic selenides and derivatives of selenophene with tetracyanoethylene (TCE) have been studied in most detail by electronic spectroscopy. The observed charge-transfer bands in the spectra of these complexes are due to electron transitions from the HOMO of the selenide to the LUMO of the TCE molecule. In most cases, the spectra of the complexes of aromatic selenides, like the spectra of the complexes of other π-donors with TCE, contain not one but two charge-transfer bonds, corresponding to electron transitions from the highest orbitals [π_s $\nu_{max}(CTB_1)$ and π_{as} $\nu_{max}(CTB_2)$, see Fig.1] of the selenide molecule to the LUMO of the acceptor molecule. The position of the maximum of the first CTB [$\nu_{max}(CTB_1)$] and its energy [$h\nu_{max}(CTB_1)$] are directly related to the energy of the HOMO and to the first ionisation potential (IP_1) of the corresponding selenide. A linear correlation between $\nu_{max}(CTB_1)$ and IP_1 was established for the complexes of TCE with selenophene and its substituted derivatives.[116,117] The complexes formed by heterocyclic compounds of selenium with TCE are more stable than those formed by the corresponding heterocyclic compounds containing sulphur.[118] For selenophenes containing different substituents in position 2, a correlation was established between the first ionisation potential and the σ_m-constants of the substituents.[119] Spectral studies of the complexes of TCE with substituted selenoanisoles, together with photoelectron spectroscopic data and quantum-chemical calculations,[39,107,120–123] established the principal regular features of the formation of the intermolecular bonds and the properties of the complexes. The nature of the electron transitions and the two observed CTB in the spectra of the complexes was examined, the regular features of the influence of electronic and steric effects on the position and intensity of the CTB were established, and the relationship between the spectral parameters and the orbital characteristics of the molecules determined. A large amount of experimental material on the complexes of TCE with substituted selenoanisoles and phenyl selenocyanates[124] established a linear relationship between the energy of the first CTB and the electrophilic σ^+-constants of the substituents.

A study of the electrochemical oxidation of substituted selenoanisoles[125] also established a linear relationship between the potential $E_{1/2}$ and the electrophilic constants of the substituents σ^+. The value of the electrochemical reaction constant ($\rho = -0.28$) was found to be practically equal to the constant found from a spectrophotometric study of the complexes of selenoanisoles with TCE ($\rho = -0.25 \pm 0.03$). This appears quite logical, since both of these methods characterise the state of the HOMO of the compounds being studied. The second charge-transfer band of the complexes of TCE with substituted selenoanisoles, unlike the first band, is little influenced by substituents,[123] and its position and energy are close to those of the CTB of the complex of TCE with benzene.

The linear relationship between $\nu_{max}(CTB_1)$ and IP_1 for TCE complexes covers a wide range of varied electron donors containing different heteroatoms, and has the form:[126]

$$IP_1\,(eV) = 5.86(\pm 0.06) + (1.31 \pm 0.03) \times 10^{-4}\,\nu_{max}(CTB_1)\,(cm^{-1}). \quad (1)$$

This equation is widely used to determine the ionisation potentials of complex heteroaromatic compounds, including selenium-containing compounds (such as arylselenoacetylenes,[127] selenides containing a carbonyl group,[107] etc.) from the measured CTB in the spectra of the complexes with TCE. Thus the electron-donor properties of selenides towards iodine (σ-acceptor) and TCE (π-acceptor) have now been fairly fully studied by electronic spectroscopy. There are extremely few published data, however, on the structural and thermodynamic parameters of complexes of selenides with other acceptors, including ν-acceptors. Calorimetric titration has been used to determine the enthalpies of formation of the complexes of a number of selenides with tine tetrachloride (with the 1:1 and 2:1 compositions),[128] aluminium tribromide,[129] and boron tribromide.[130] The enthalpy of formation of the complex $(CH_3)_2Se.Ga(CH_3)_3$ has been determined by the gas dissociation method.[131] The values of $-\Delta H$ (kcal $mole^{-6}$) for a number of complexes of selenides with aluminium tribromide and tin tetrachloride are given in Table 3. The selenides form fairly stable complexes with these acceptors. Studies of the complex-forming power of bis-selenides of the type $RSe(CH_2)_nSeR$ towards PT and Pd salts by ^1H, ^{77}Se, and ^{195}Pt NMR, ultraviolet, and IR spectroscopy made it possible to solve various problems of the stereochemistry of the complexes formed and to determine the relationship between the parameters found.[132] ^1H NMR and IR spectroscopy established the formation of H-complexes of a number of selenides with phenol.[133-135]

Analysis of the results of an IR Fourier spectroscopic study of the complex $H_2Se.HF$ in an argon matrix led to the conclusion that it has a pyramidal structure,[136] which is consistent with the view that the $4p^2$-LPE of the selenium atom takes part in the formation of an intermolecular H-bond. Non-empirical quantum-chemical calculations for the complex $H_2Se.HCN$ [137] also indicate that it has a pyramidal structure.

A detailed study of the IR and Raman spectra of the complex $(C_2H_5)_2Se.HCl$ in argon and nitrogen matrices revealed fine effects due to conformational isomerism. The different rotational isomers of diethyl selenide react with HCl to give complexes with different stability.[57] In addition to the 1 : 1 complexes, 1 : 2 complexes with branched H-bonds were detected. The formation of complexes with the same composition was also established in the reaction of diethyl selenide with HCl in CCl_4.[138] It was concluded that the H-bond in the complex in the argon matrix is stronger than that in an inert solvent.

The high sensitivity of the chemical shift in the ^{77}Se NMR spectra has been used successfully to study complex formation by phenyl selenylacetate with the enzyme α-chymotrypsin. The composition of the complex (1 : 1) was established, and its dissociation constant determined.[139] Thus organic compounds of selenium, like the corresponding compounds of the other elements of the oxygen subgroup of group VI form fairly stable complexes with various acceptors. To estimate the degree of similarity and difference in the electron-donor properties of these compounds, various parameters of the complexes which they form can be compared. The most reliable characteristic of the complex-forming power of a given donor towards a given acceptor is the enthalpy of formation of the complex. The enthalpies of formation $-\Delta H$ (kcal mole^{-1}) of a number of 1 : 1 complexes are given below.[129,130,135,140] There are practically no published quantitative data on the complex-forming power of tellurium(II) compounds.

Donor	Acceptor				
	I_2	BBr_3	$AlBr_3$	$SnCl_4$	C_6H_5OH
$(C_2H_5)_2O$	4.3	18.8	36.5	5.8	5.9
$(C_3H_7)_2S$	8.1	22.8	31.1	12.6	4.2
$(C_3H_7)_2Se$	9.7	22.8	29.9	14.6	3.7

Thus the order of change in the values of $-\Delta H$ in the series ethers – sulphides – selenides is different for the reactions with different acceptors.

As noted above, the electron-donor properties of molecules are determined to a large extent by the energy state of the HOMO, given by the first ionisation potential. For the compounds RER^1 of the elements of the oxygen sub-group, the values of IP_1 (eV) are as follows:

R	R^1	O	S	Se	Te
—	—	13.6	10.4	9.75	9.01
CH_3	CH_3	10.0	8.65	8.40	7.89
C_6H_5	CH_3	9.29	8.07	7.99	7.60
C_6H_5	C_6H_5	8.09	7.80	7.79	—

The values of IP_1 decrease with increase in the principal quantum number of the element, in the order O > S > Se > Te. A large change is observed on going from the oxygen compounds to the sulphur compounds, and the differences in the IP_1 values for the sulphur and selenium compounds are much smaller. Judging from the IP_1 values, the donor properties of the compounds of the elements of group VI should increase in the following order: O < S < Se < Te. This order is not always observed, however, This can be clearly seen by comparing the order of change in the values of $-\Delta H$ for the complexes of ethers, sulphides, and selenides with iodine (Se > S > O) and with phenol (O > S > Se). Of considerable importance in the formation of the intermolecular bond are the conditions of overlap of the interacting orbitals—the HOMO of the donor molecule and the LUMO of the acceptor molecule.

The overlap integrals of the corresponding orbitals (indicated in brackets) for a number of model donor–acceptor bonds are given below:[130,140]

Acceptor	Donor			
	R_2O ($2sp^2$)	R_2S ($3p$)	R_2Se ($4p$)	$R_3P{=}Se$ ($4p$)
I ($5p$)	0.27	0.34	0.41	0.47
B ($2sp^2$)	0.34	0.46	0.41	0.50
Al ($3sp^2$)	0.40	0.38	0.43	—
Sn ($5sp^2d$)	0.76	0.60	0.63	—
OH ($1s$)	0.43	0.36	—	—

The order of change in the overlap integrals for the complexes of the oxygen, sulphur, and selenium compounds with iodine agrees with the order of change in IP_1, so that the enthalpy of formation of the complexes of I_2 with the selenides should be greater than for the sulphides and ethers, as observed experimentally. For the complexes with compounds of boron, aluminium, and tin, the order is slightly different, and this is reflected in their enthalpies of formation. An important part in the formation of intermolecular bonds is played by steric effects. These decrease with increase in the size of the central atom of the donors indicated (O > S > Se), and for the above acceptors they are most clearly revealed in the complexes $D.BBr_3$ and $D.SnCl_4$. Thus the order of change in the electron-donor properties of a given series of compounds is determined by a number of factors, and may be different for the reactions with different acceptors.

III. THE STRUCTURE AND COORDINATION PROPERTIES OF COMPOUNDS OF THE TYPE $R_nE{=}Se$

The intensive development of the chemistry of selenium in recent years has drawn the attention of research workers to the selenium analogues of ketones, phosphine oxides, and carboxylic acid amides, that is compounds containing E = Se bonds. Of these, the compounds containing $\geqslant P{=}Se$ and $\geqslant C{=}Se$ bonds have been most fully studied. Structural studies have shown that the phosphorus atom in selenophosphoryl compounds (Table 4) is at the centre of a slightly distorted tetrahedron; the average values of the SePC and CPC valence angles are 111 – 114° and 103 – 106° respectively. The rings of the aromatic fragments of the compounds studied are rotated relative to one another; the angles made by the plane of the ring with the C – P – Se plane are different compounds, and also vary over a wide range for different rings in the same compound, for example from 13° to 56° in compound (XVII). An exception is the fairly symmetrical (C_3) structure of the molecule of tris(2-furyl)-phosphine selenide (XX); the angles made by all three furyl groups with the C – P – Se plane in this compound are almost identical, and the torsional angles O – C – P – Se are 48.2, 46.3, and 46.7°. A noteworthy feature is the relatively large difference in the lengths of the C – P and P = Se bonds for different phosphine selenides. The observed differences have been attributed to the influence of steric effects [for example for compounds (XVII) and (XVIII)], the inductive effect of the substituents [for compounds (XVIII) and (XIX)], and the ability to form $C_{(2p)\pi}-P_{(3d)\pi}$ bonds. Thus according to Ref.145, the fact that the C – P bond in the molecule of tris-(2-furyl)phosphine selenide (XX) is shorter than that in other triarylphosphine selenides is due to the increase in the extent of the $C_{(2p)\pi}-P_{(3d)\pi}$ interaction resulting from the stronger σ-electron-acceptor properties of the 2-furyl group compared with the phenyl group. The fact that the P = Se bond in compounds (XIX) and (XX) is shorter than in compounds (XVI) – (XVIII) has also been attributed to the σ-electron-acceptor properties of the trifluoromethylphenyl or furyl groups and the consequent increase in the *s*-character of the orbital of the P atom in the bond with Se.[145,149]

The vibrations of the $\geqslant P{=}Se$ bond are not characteristic, and vary over a wide range, depending on the composition and structure of the substituents on the phosphorus atom. Thus for compounds

of the type $R_3P=Se$, the vibrational wavenumbers assigned to the P=Se bond are:[150]

R_3	$(CH_3)_3$	$(C_2H_5)_3$	(cyclo-C_6H_{11})$_3$	$(C_6H_5)_3$
$\nu_{P=Se}$ (cm^{-1})	441	422	543	560

According to Raman spectroscopic data, the values of $\nu_{P=Se}$ for the compounds $(C_6H_5)_2P(Se)CH_2-P(X)(C_6H_5)_2$ vary in the range 525–535 cm^{-1} for X = O, S, Se, or the LPE of the P atom.[151]

Table 4. Structural parameters of compounds containing $\geqslant P=Se$ and $\geqslant C=Se$ bonds.

Compound	Bond length, Å C–P, P = Se, or C = Se	Angle C–P–Se, °	Refs.
$(C_6H_5)_3P=Se$ (XVI)	1.826; 2.106	—	[141]
$(2\text{-}CH_3C_6H_4)_3P=Se$ (XVII)	1.834; 2.116	112.7	[142]
$(3\text{-}CH_3C_6H_4)_3P=Se$ (XVIII)	1.820; 2.109	—	[143]
$(3\text{-}CF_3C_6H_4)_3P=Se$ (XIX)	1.815; 2.094	113	[144]
$(2\text{-}C_4H_3O)_3P=Se$ (XX)	1.778; 2.094	114.9	[145]
$4\text{-}(CH_3)_2NC_6H_4P(=Se)(CH_3)_2$ (XXI)	1.82; 2.105	113.3	[146]
$CH_2=C=Se$ (XXII)	— 1.706	—	[147]
O=C=Se (XXIII)	— 1.7098	—	[147]
S=C=Se (XXIV)	— 1.695	—	[147]
HN=C=Se (XXV)	— 1.717	—	[147]
$CH_3N=C=Se$ (XXVI)	— 1.708	—	[147]
$C_2H_5N=C=Se$ (XXVII)	— 1.709	—	[148]

For compounds with different substituents on the phosphorus atom, such as $(C_2H_5)_2ClP=Se$ [152] or $(RO)_nR_{3-n}P=Se$ (n = 1–3; R = CH_3, C_2H_5),[153,154] the spectra show splitting of the $\nu_{P=Se}$ bands, attributed to the presence of rotational isomers. The ratio of the intensities of the corresponding bands can be used to determine the relative concentration of the isomers in the mixture and the thermodynamic parameters of the equilibrium.[154]

A study of the electronic spectra of compounds R′R″R‴P=Se [155] showed that the selenophosphoryl group, like the thiophosphoryl group, has chromophoric properties. The relationship between the position of the long-wave band (230–280 nm), assigned to a $n-\pi^*$ transition, and the nature of the substituents on the phosphorus atom has been studied.

Extremely important characteristics of a chemical bond are its polarity, polarisability, and the anisotropy of the polarisability. The P=Se bond is fairly polar; the magnitude of its dipole moment depends on the nature of the substituents, and for compounds of the type $R_3P=Se$ has the following values:[156]

R_3	$(C_6H_5)_3$	$[(CH_3)_2N]_3$	CH_3Cl_2
$\mu_{P=Se}$ (D)	3.73	3.88	2.89

A linear correlation is observed between the dipole moments of the P=Se bond and the inductive constants of the substituents.[156] Measurements of the dipole moments and the Kerr effect have been used to determine the polarisability and the anisotropy of the polarisability of the P=Se bond in the cyclic selenophosphate $CH_3-C(CH_2O)_3P=Se$.[157]

Vaulable information on the nature of the P=Se bond has been obtained by ^1H, ^{31}P, and more particularly ^{77}Se NMR.[145,149,151,158,159] The values of the chemical shifts δ ^{77}Se and the spin–spin coupling constants $^1J(^{31}P-^{77}Se)$ depend to a significant extent on the nature and stereochemistry of the substituents on the phosphorus atom. Electron-acceptor substituents in compounds of the type $R_3P=Se$ lead to an increase in $^1J(^{31}P-^{77}Se)$, whereas electron-donor and bulky substituents decrease it.[159] For a number of compounds $(XC_6H_4)_3P=Se$, a linear relationship has been established between $^1J(^{31}P-^{77}Se)$ and the constants of the substituents.[158]

The spin–spin coupling constant between directly bonded atoms is increased chiefly by the Fermi-contact interaction of the moment of the nucleus and the spin of the electron of the *s*-orbital. This made it possible to examine the observed changes in the values of $^1J(^{31}P-^{77}Se)$ in a series of analogous compounds in relation to the influence of the substituents on the population of the 3*s*-orbital of the phosphorus atom.[145,159] The $^1J(^{31}P-^{77}Se)$ values for compounds of the type $Ar_3P=Se$ indicate that the 2-thienyl and 2-furyl groups in the corresponding phosphine selenides are electron-accepting.[145,159]

Stable compounds containing C=Se bonds were obtained comparatively recently,[160–162], and have been less extensively studied. Structural studies have shown that the C=Se bonds, like the P=Se bonds (see Table 4) have similar lengths in different compounds; the differences do not exceed ±0.01 Å.

The NMR spectra of organoselenium compounds containing C=Se bonds have shown that the ^{77}Se chemical shift has an unusually high sensitivity to the electronic state of the selenium atom.[161–163] The values of δ ^{77}Se for a number of compounds of this type are much greater, sometimes by ~2000 p.p.m., than δ ^{77}Se for dimethyl selenide, and are extremely sensitive to the structural and electronic characteristics of the molecules.[161] The ^{13}C and ^{77}Se NMR spectra of a number of heterocyclic compounds containing C=Se bonds show that δ (C=^{77}Se) is much more sensitive (by a factor of more than 70) to the influence of structural and electronic effects than δ (^{13}C=Se).[163] Thus ^{77}Se NMR opens up extensive possibilities for studying the structure of organoselenium compounds of this type. Published data on the coordination properties of compounds of the type $R_nE=Se$ relate chiefly to compounds containing $\geqslant P=Se$ bonds. The $\nu_{P=Se}$ band in the IR spectrum is displaced to lower wavenumbers on complex formation. The magnitude of the displacement depends on the composition and structure of the phosphine selenide molecules, and also on the properties of the acceptor. Thus for the complexes of triphenylphosphine selenide with tantalum pentafluoride[164] and iodophenylacetylene,[165] $\Delta\nu_{P=Se}$ had the values 20 cm^{-1} and 21 cm^{-1} respectively. A displacement of the $\nu_{P=Se}$ band by 13–14 cm^{-1} has been observed in the spectra of the complexes of various bidentate phosphine selenides with mercury thiocyanate.[166] Ultraviolet (UV) spectroscopy and calorimetry have been used to determine the thermodynamic parameters of complex formation by phosphine selenides with I_2 [167,168] and $SnCl_4$.[167,169] The enthalpies of formation ($-\Delta H$, kcal $mole^{-1}$) of the 1:1 complexes studied are given below; the values of $-\Delta H$ for the corresponding complexes with $R_3P=O(S)$ are given for comparison:

Donor	Acceptor I_2	Acceptor $SnCl_4$	Donor	Acceptor I_2
$(C_4H_9)_3P=O$	6.4	25.8	$[(CH_3)_2N]_3P=O$	7.3
$(C_4H_9)_3P=S$	9.0	15.6	$[(CH_3)_2N]_3P=S$	8.1
$(C_4H_9)_3P=Se$	13.0	15.4	$[(CH_3)_2N]_3P=Se$	12.5

Thus phosphine selenides form fairly stable complexes with I_2 and $SnCl_4$. The donor properties of the selenium atom in the compounds $R_3P=Se$ are slightly stronger than in the corresponding compounds R_2Se. The relative complex-forming power of the series of compounds $R_3P=X$, where X = O, S, Se, judging from the $-\Delta H$ values for the complexes with I_2, is given by the sequence Se > S > O. The same order was found by UV spectroscopy for the complexes with I_2, ICl, and IBr.[170] The opposite order is observed for the complexes with tin tetrachloride: O > S ⩾ Se. The values of $\Delta\nu_{OH}$ and $\Delta\nu_{NH}$ in the IR spectra of a number of proton donors (naphthol, phenol, pyrole, halogenated alcohols) in their reaction with the compounds $(C_6H_5)_3P=O(S)(Se)$ showed that

their ability to form H-complexes also decreases in the order O > S > Se.[171] Since the differences in the influence of steric factors in complex formation involving these compounds are apparently small, the reversal of the order of their donor properties in the H-complexes and the complexes with $SnCl_4$, compared with I_2, is apparently related chiefly to the conditions of overlap of the interacting orbitals of the molecules of the donor and acceptor, as noted above. The complexes of phosphine selenides of the series $(C_6H_5)_n.(C_4H_9)_{3-n}P{=}Se$ (n = 1–3) with HgX_2 and CdX_2 (X = Cl, Br) have been studied by ^{31}P NMR.[172] The spin–spin coupling constant $^1J(^{31}P-^{77}Se)$ decreases on complex formation, in agreement with IR spectroscopic data ($\Delta\nu_{P=Se}$).

There are almost no published data on the electron-donor properties of compounds containing P=Se bonds. UV spectroscopy has been used to study complex formation by a number of cyclic selenoamides with iodine.[173] The temperature dependence of the equilibrium constants was used to determine the enthalpies of formation of the complexes, which vary over a fairly wide range (6.0–12.0 kcal mole^{-1}), depending on the substituents.

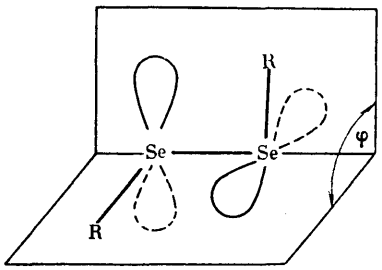


Figure 2. Spatial structure of organic diselenides.[177]

Table 5. Structural parameters of diselenides.

Diselenide	r, Å C–Se, Se–Se		Angle C–Se–C, °	θ, °	Method	Refs.
$(CH_3Se)_2$ (XXVIII)	1.954	2.326	98.9	87.5	ED	[174]
$(CF_3Se)_2$ (XXIX)	2.018	2.292	98.0	—	ED	[175]
$[(C_6H_5)_2CHSe]_2$ (XXX)	1.97	2.285	100.1	82	XRD	[176]
$(C_6H_5Se)_2$ (XXXI)	1.93	2.29	106±2	82	XRD	[177]
$(C_6F_5Se)_2$ (XXXII)	1.910	2.319	98.7	75.3	XRD	[178]
$(4\text{-}CH_3C_6H_4Se)_2$ (XXXIII)	1.915	2.328	101.6	80.3	XRD	[179]
$(4\text{-}ClC_6H_4Se)_2$ (XXXIV)	1.93	2.333	101.1	74.5	XRD	[180]
 (XXXV)	1.910	2.364	—	—	XRD	[181]

IV. THE STRUCTURE AND ELECTRON-PROPERTIES OF DISELENIDES

Diselenides R–Se–Se–R, like other compounds of the oxygen sub-group with dielement bonds, have a skewed conformation (Fig.2). Structural data (Table 5) show that the interplanar angle C–Se–Se/Se–Se–C (θ) is 75–90°, depending on the composition and structure of R. The Se–C_{sp^3} bond lengths (1.95–2.02 Å) in the molecules of aliphatic diselenides are longer than the Se–C_{sp^2} bond lengths (1.91–1.93 Å) in aromatic diselenides (Table 5). The reason for the observed differences is apparently analogous to that examined above in the analysis of the bond lengths in monoselenides. The Se–Se bond lengths depend on the composition and structure of the groups R, vary over a fairly wide range from 2.28 Å to 2.33 Å for the diselenides indicated in Table 5, and differ from the value 2.34 Å for the length of the ordinary Se–Se bond in elemental selenium.[182]

The main factors responsible for the skewed conformation of diselenides (Fig.2) are: a) the mutual repulsion of the $4p^2$ lone pairs of electrons of the selenium atoms; b) the possibility of additional $p_\pi-d_\pi$ Se–Se bonding; and c) the mutual repulsion of the groups R. Quantum-chemical calculations of the barrier to rotation relative to the diselenide bond in dimethyl diselenide, carried out by the CNDO/2 method with optimisation of the geometry[183] and by the expanded Hückel method,[184] and also non-empirical calculations using different basis sets,[185] showed that they are fairly high. Thus according to these data, the energy of the conversion of the skewed conformation (θ ≃ 90°) into the *cis*-form (θ = 0°) has the values 6,[184] 11.19,[185] or 18.09 [2185] kcal mole^{-1}, and the energy of the conversion into the *trans*-form (θ = 180°) has the values 3,[184] 4.86,[185] or 11.51 [185] kcal mole^{-1}. Analogous calculations of the barrier to rotation relative to the diselenide bond in the $CF_3Se-SeCF_3$ molecule gave the values 45 kcal mole^{-1} for the *cis*-form and 15 kcal mole^{-1} for the *trans*-form.[184] The determination of the barriers to rotation (kcal mole^{-1}) from the temperature dependence of the ^1H NMR spectra of a number of aromatic diselenides gave the following results:

$C_6H_5CH_2Se-SeC_6H_5$	6.3	[186]
$(C_6H_5CH_2)_2Se_2$	<5.6	[186]
$[2,4,6\text{-}(t\text{-}C_4H_9)_3C_6H_2]_2Se_2$	12.5	[187]

The barrier to rotation in the diselenides is ~20% lower than that in the corresponding disulphides.[186] The greater length of the Se–Se bond, compared with that of the S–S bond, apparently decreases the interaction in the diselenide bond, compared with the disulphide. This can explain the lower stability of polyselenides (for example triselenides) compared with polysulphides. It has been suggested[188] that bulky groups such as $[(CH_3)_3Si]_3C$ can stabilise polyselenide bridges. The structure of the triselenide $[(CH_3)_3Si]_3C-Se-Se-Se-C[Si(CH_3)_3]_3$ has been determined.

The measured dipole moments of aromatic diselenides[189–193] indicated that in inert solvents, as in the crystalline state, the diselenides have a coiled conformation; the dihedral angle is 72–85°. The temperature dependence of the dipole moments of diphenyl diselenide and its symmetrically disubstituted derivatives (CH_3, F, Br) confirmed the skewed conformation of the molecules in solution (benzene, 298°) and slight oscillation or rotation of the ArSe groups about the Se–Se bond with increase in temperature.[191] The dipole moments and Kerr constants of disubstituted diphenyl diselenides were used to estimate not only the dihedral angles θ but also the angles of rotation of the phenyl rings (Φ) relative to the C–Se–Se plane in the diselenides studied.[190,192] When electron-donor substituents ($N(CH_3)_2$, OCH_3, CH_3) are introduced into the 4 and 4′ positions of the phenyl rings, the angle Φ increases in proportion to the electron-donor strength of the substituent. On the other hand, strong electron-acceptor substituents (for example NO_2) lead to flattening of the $4\text{-}NO_2C_6H_4Se$ fragment (angle Φ ≃ 0). A linear relationship was established between $\cos^2\Phi$ and σ^+ for the substituent. The dependence of the observed increase in the polarisability of diaryl diselenides on the nature of the substituent has been interpreted in terms of possible conjugation of the two aromatic fragments through the dislenide bridge.[189,192] The possible interaction of the π-electron system of the phenyl rings with the diselenide bridge is indicated by the results of quantum-chemical calculations (Del Re, SSP-PPP), the dipole moments, and the magnitude of the π-charges on the atoms of diphenyl diselenide and a number of

its 4,4′-disubstituted derivatives.[194] Evidence of intramolecular π-electron interaction involving the diselenide bridge of diaryl diselenides is provided by the dependence of the observed changes in the integral intensity of the absorption bands of the Se–Se bond in the Raman spectra on the nature and position (*ortho*, *meta*, *para*) of the substituents.[195] Electron-donor substituents, which increase the electron density of the diselenide bond and hence its polarisability, lead to an increase in the intensity of the corresponding band in the Raman spectrum. For the substituents CH_3, OCH_3, and $N(CH_3)_2$, its value was greatest for 4,4′-dimethylaminodiphenyl diselenide. The decrease in intensity on going from the *para*- to the *ortho*- or *meta*-substituted diphenyl diselenides indicates a decrease in the degree of interaction of the $p\,\pi$-conjugation type between the diselenide bridge and the substituents in the isomer order indicated.[195] Evidence of $p\,\pi$-electron interaction between the diselenide bridge and the aromatic fragments of diaryl diselenides is also provided by the observed linear dependence of the intensity of the Raman bands assigned to the Se–Se bond on the angle of rotation of the phenyl ring. The vibrational wavenumbers of the Se–Se bond for different dislenides lie in the range 270–300 cm^{-1}.[195–200]

The UV spectra of aliphatic diselenides contain one absorption band at about 310 nm.[201] The appearance of this band is usually attributed to an electron transition from the HOMO, formed by a n^--combination of the atomic orbitals of the LPE of the selenium atoms, into the antibonding σ*-orbital of the diselenide bridge. The UV spectra of aromatic diselenides contain three absorption bands at ~250, 270, and 330 nm.[202] The spectral characteristics of the long-wave band are apparently analogous to those of the band observed in the spectra of aliphatic diselenides. The electron transitions at shorter wavelengths are analogous to the absorption bands of selenoanisole, and are probably due to the transfer of electron density from the diselenide bridge to the aromatic fragments.

The formation of the molecular orbitals and the nature of the electron transitions in aromatic diselenides and their isologues were examined in Ref.202.

Valuable information on the nature of the intramoelcular electronic interactions in diselenides has been obtained by ^{77}Se NMR,[203,204] and more particularly by combined ^{13}C and ^{77}Se NMR studies.[205] Comparison of the value of δ $^{13}C(4)$ and δ $^{13}C(3, 5)$ of diphenyl diselenide with δ ^{13}C for benzene showed that the C_6H_5. .SeSe group behaves as both a π-donor and a δ-acceptor towards the phenyl ring, increasing the shielding of C(4) and decreasing the shielding of C(3, 5). The specific features of the influence of substituents in the phenyl rings on the shielding of the selenium atoms of diselenides have been established.[205]

There are extremely few published data on the complex-forming power of diselenides. Spectrophotometry has been used to study complex formation by a number of 4,4′-disubstituted diphenyl diselenides with iodine in heptane.[206,207] Irrespective of the component ratio in the solution, the diaryl diselenides react with I_2 to form 1 : 1 complexes. In contrast to this, in the dimethyl diselenide–I_2 system, 1 : 2 complexes are formed in addition to the 1 : 1 compounds.[206] The difference in the behaviour of the dialkyl and diaryl diselenides in their reactions with I_2 to some extent reflects the difference in their electronic states. Calculations of the electron density distribution by the Del Re and HMO methods showed that the effective (σ + π) electronic charge on each selenium atom of the diphenyl diselenide molecule is much lower than the σ-charge on the selenium atom in the dimethyl diselenide molecule.[206] The results of this calculation indicate that the localisation of electron density on the selenium atoms is greater in dimethyl diselenide than in diphenyl diselenide. This on the one hand confirms the $p\,\pi$-conjugation in aromatic compounds of selenium and on the other hand explains the differences in the donor properties of aromatic and aliphatic diselenides.

Spectrophotometry has been used to study complexes of diphenyl diselenide and its disubstituted derivatives with tetracyanoethylene.[207,208] 1 : 1 complexes are formed in the systems studied. The spectra of the complexes, like the spectra of the complexes of TCE with diaryl monoselenides, contain two CTB. The position of CTB_1 depends on the nature of the substituents in the aromatic fragments. A linear relationship was established between $h\nu_{max}(CTB_1)$ and $\Sigma\sigma^+$. The position of CTB_2 is approximately the same in the spectra of all the complexes (380–390 nm). The spectral characteristics of the complexes of TCE with diaryl diselenides were used, in accordance with Eqn.(1), to estimate the ionisation potentials of the latter. The ionisation potentials were obtained for a large group of *p*-disubstituted diphenyl dislenides. The ionisation potential of diphenyl diselenide, found from the correlation equation (1) (8.2 eV),[208], shows good agreement with the value of IP_1, 8.3 eV, determined by PES.[193] PES has been used to determine the ionisation potentials of a number of compounds with dielement bonds, of the type $(CH_3)_2XYCH_3$, where X = P, As; Y + S, Se. The experimental IP_1 values have been compared with the calculated (CNDO/2) energies of the HOMO. The first two PES bands are due to the removal of electrons from orbitals which are linear combinations of orbitals occupied by the LPE of the corresponding heteroatoms.[209]

The heat of formation of the complex of diphenyl diselenide with phenol has been estimated by IR spectroscopy. The donor properties of the selenium atom in the diselenide are much weaker than in the monoselenide: 1.9 kcal $mole^{-1}$ and 3.3 kcal $mole^{-1}$ respectively.[135]

Table 6. Ionisation potentials of diselenides (eV) and the dipole moments (μ_c, D) and enthalpies of formation ($-\Delta H_c^0$, kJ $mole^{-1}$) of their complexes with $GaCl_3$ (benzene, 298 K).[210]

Complex	IP_1 diselenide (Ref.207)	μ_c	$-\Delta H_c^0$
$(4\text{-}CH_3C_6H_4)_2Se_2\cdot GaCl_3$	8.07	8.6	87
$(C_6H_5)_2Se_2\cdot GaCl_3$	8.21	7.5	82
$(4\text{-}FC_6H_4)_2Se_2\cdot GaCl_3$	8.28	—	80
$(4\text{-}ClC_6H_4)_2Se_2\cdot GaCl_3$	8.28	6.2	79
$(4\text{-}BrC_6H_4)_2Se_2\cdot GaCl_3$	—	6.5	77

Cryometric, calorimetric, and dielectric constant measurements have been used to study complex formation by a number of diaryl diselenides with gallium trichloride. Irrespective of the reagent ratio in these systems, the 1 : 1 complexes are formed. Only one of the selenium atoms of the diselenide bridge forms a donor–acceptor bond with the gallium halide. The high values of the dipole moments and the heats of formation of the complexes (Table 6) indicate that they are *nv*-complexes, like the complexes formed by monselenides with aluminium tribromide.[129] Table 6 shows that the donor properties of the selenium atom in diaryl diselenides, characterised by the $-\Delta H_c^0$ values, depend on the nature of the substituents in the ring. Electron-donor substituents (CH_3) increase the strength of the intermolecular Se → Ga bond, and halogen atoms (F, Cl, Br) decrease it. Although the data are limited, the relationship between the $-\Delta H_c^0$ values and the constants σ of the substituents can be followed.[210] A correlation is also observed between the $-\Delta H_c^0$ values and the ionisation potentials the diselenides, obtained from spectrophotometric data for the charge-transfer complexes (CTC) with TCE.[207] An attempt to determine the thermodynamic parameters of complex formation by diaryl diselenides with the stronger

acceptor aluminium tribromide led to the discovery of a new method for generating and stabilising selenium-containing radicals (see below).

Thus published data on the coordination properties of organic diselenides indicate that only the first steps have been taken in this field.

Table 7. *g*-Values and line widths (G) in the EPR spectra of diaryl diselenide–aluminium tribromide–benzene systems at 298 K.[210]

Diselenide	Signal No. in the EPR spectrum		
	I	II	III
$(C_6H_5)_2Se_2$	2.0761 (23.75)	2.0300 (9.60)	2.0021 (1.67)
$(4\text{-}FC_6H_4)_2Se_2$	2.0694 (17.50)	2.0332 (5.83)	2.0025 (6.25)
$(4\text{-}ClC_6H_4)_2Se_2$	2.0730 (23.30)	2.0380 (11.70)	2.0027 (5.42)
$(4\text{-}BrC_6H_4)_2Se_2$	2.0744 (24.17)	2.0319 (12.50)	2.0026 (4.58)

V. SELENIUM-CONTAINING FREE RADICALS

Free radicals containing an unpaired electron on a selenium atom have been little studied. Until recently, the possible participation of selenium-centred radicals in chemical reactions was doubted. Thus in a published review[2] it was noted that there is very little published information on the preparation and chemistry of organoselenium radicals, and from its analysis it was concluded that there is no convincing proof that organoselenium radicals take part in the processes examined. A similar conclusion that the existence of organoselenium radicals has not been proved was reached in Ref.211. At the same time, photochemical reactions involving organoselenium compounds are acquiring increasing importance in present-day organic synthesis, and the mechanism of these reactions is discussed in terms of the formation of selenium-centred radicals.[212] Selenium-centred radicals have been detected by EPR in the low-temperature photolysis of a number of organic selenides and diselenides;[213–215] determination of the *g*-values showed that they are greater for radicals containing selenium (2.095–2.099) than for sulphur-containing radicals (2.06).[214] The EPR spectrum of the photolysis products of organoselenium compounds in a number of cases are much more complex than the corresponding spectra of the sulphur compounds. It has been shown that, in contrast to sulphur compounds, the photolysis and radiolysis of various selenium compounds, in particular diselenides, are accompanied by the rupture of not only the Se–Se bond but also the C–Se bond, to give the radicals R$^{\cdot}$, RSe$^{\cdot}$, and RSe–Se$^{\cdot}$.[213,215,216] This distinguishes the photochemistry of the diselenides from that of the disulphides, where only the S–S bond is broken, to give RS$^{\cdot}$ radicals. Interesting results were obtained in a study of the photolysis of a number of selenides and diselenides in the presence of nitrosodurene, used to trap radical species.[217] In a number of systems, EPR detected the selenylnitroxide radical. The mechanism of the process was found to depend on the composition and structure of the organoselenium compound. Thus dibenzyl diselenide and diphenyl diselenide react differently on ultraviolet irradiation in the presence of nitrosodurene; the C–Se bond is broken in the first compound, and the Se–Se bond in the second.[217] In addition, studies of the photochemical reactions of a number of diselenides with tertiary phosphines[218,219] showed that, irrespective of the nature of R in the R_2Se_2 molecule (CH_2, C_2H_5, $CH_2C_6H_5$, C_6H_5) and the composition of the phosphine [$CH_3(C_6H_5)_2P$, $(CH_3)_2C_6H_5P$, $(C_6H_5)_3P$], the reaction

$$R_2Se_2 + Ar_3P \xrightarrow{h\nu} R_2Se + Ar_3P{=}Se$$

takes place by a chain mechanism, and the first stage in all cases is the rupture of the diselenide bond. This reaction has been recommended as a method for synthesising the corresponding selenides, and phosphine selenides, since it gives almost quantitative yields of the products under mild conditions.

Thus organoselenium free radicals, like the sulphur-containing radicals, formed by photolysis and radiolysis, are unstable. They are detected only at low temperatures in solid matrices. The stability of free radicals is usually increased by increasing the delocalisation of the electron spin density, and also by steric shielding of the atoms carrying the unpaired electron.[211] Complex formation has been proposed[220–222] as a new effective method for generating and stabilising free radicals containing a heteroatom. Thus stable sulphur-containing radicals of the type $ArS^{\cdot}.MX_3$ were obtained for the first time by the reaction of diaryl disulphides with strong electron acceptors (aluminium and gallium halides). The formation of these radical complexes results from the decrease in the strength of the disulphide bond on complex formation, and the homolytic rupture of the bond when the interactions are sufficiently strong. Quantum chemistry has shown that the free electron of the radical complex is localised chiefly on the sulphur atom. The properties and reactivity of a number of radical complexes $RS^{\cdot}.MX_3$ have been studied.[223,224] Studies of similar reactions of diaryl diselenides with aluminium tribromide and gallium trichloride in benzene or cyclohexane[210,225] have shown that the first stage is the formation of 1:1 donor–acceptor complexes. This stage, like all complex-formation reactions, is very rapid. The second stage, leading to the rupture of the corresponding bonds with the addition of a second molecule of the halide to the 1:1 complex, is slower. Its rate depends on the nature of the acceptor and the aryl fragment of the diselenide. As noted above, the relatively low rate of the second stage of the reaction of diaryl diselenides with gallium trichloride made it possible to measure the heat of formation and dipole moments of the complexes $Ar_2Se_2.GaCl_3$, formed in the first stage.[210] Freshly prepared benzene solutions of the complexes of diaryl diselenides with gallium trichloride do not give signals in the EPR spectra. When solutions containing an excess of gallium trichloride are left to stand, a brightly coloured oil separates, and signals appear in the EPR spectra, indicating the presence of paramagnetic species. In the reaction of diaryl diselenides with a stronger electron acceptor (aluminium tribromide) in benzene or cyclohexane, the separation of paramagnetic products is observed when the components are mixed. The EPR spectra of Ar_2Se_2–$AlBr_3$–benzene systems contain three singlets. The high *g*-values of the singlets I (~2.070) and II (~2.030) differ considerably from the *g*-value of the free electron (2.0023); the large line width makes it possible to assign them to radicals containing a heavy atom, in this case selenium. In view of what has been said on the possible rupture of the C–Se and Se–Se bonds in the diaryl diselenide molecule, the observed singlet I ($g \simeq 2.07$) was assigned to the radical complex $ArSeSe^{\cdot}.AlBr_3$, and the singlet II ($g \simeq 2.03$) to the radical complex $ArSe^{\cdot}.AlBr_3$. This assignment was confirmed by the signal in the EPR spectrum of the $(C_6H_5)_2Se$–$AlBr_3$–benzene system, where only the rupture of the C–Se bond is possible, to give the radical complex $C_6H_5Se^{\cdot}.AlBr_3$. The spectrum of this system contains a singlet with a *g*-value of 2.034, which was assigned to singlet II (the radical complex $C_6H_5Se^{\cdot}.AlBr_3$). The *g*-value and the form of the third singlet in the EPR spectra of Ar_2Se_2–$AlBr_3$–benzene systems differ from those of the singlets assigned to the selenium-centred radicals. The *g*-value, which is close to that of the free electron, indicates that this singlet is due to a stabilised hydrocarbon radical, formed by the homolytic rupture of the C–Se bond.

The proposed mechanism of the reaction of diaryl diselenides with aluminium tribromide was confirmed by gas–liquid chromatography (GLC). The displacement of the radicals from the complexes formed in the $(C_6H_5)_2Se_2-AlBr_3-$benzene system by a stronger donor (D = $(C_2H_5)_2O$, H_2O) gives the complexes D.$AlBr_3$ and the products of the reaction of the displaced free radicals. GLC showed that the reaction mixture contains diphenyl diselenide, diphenyl selenide, and diphenyl. Other products, including C_6H_5SeH and C_6H_5Br, were not detected. Like the thiyl radical complexes Ar$^{\cdot}$.MX_3, the selenium-containing radical complexes are highly stable; the EPR spectra of specimens in sealed ampoules (in the absence of moisture) remain unchanged for a long time (several months). By analogy with the radical complexes ArS$^{\cdot}$.MX_3,[223] the stability of the organoselenium radical complexes is apparently due to the following effects: a) a decrease in the electron density on the selenium atom on formation of a donor–acceptor bond involving a lone pair of electrons of the selenium atom and a vacant orbital of the metal atom, and a consequent lowering of the level of the orbital of the unpaired electron; b) the steric shielding, by the acceptor molecule MX_3, of the selenium atom carrying the free electron.

The formation of radical complexes by the reaction of diaryl diselenides with the halides of group III metals has been observed not only when the reaction is carried out in solution, but also when the components are fused together. The EPR spectra indicate that the nature of the radical complexes formed is the same for the reactions in the melt and in solution.[210]

Thus complex formation by diaryl selenides and diaryl diselenides with strong electron acceptors can provide a source of stable selenium-centred radicals.[210,225]

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Organosilathianes

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Published data on the synthesis and physical and chemical properties of organosilathianes have been summarised and systematised, and the possibilities for their practical application examined and evaluated.
The bibliography contains 215 references.

CONTENTS

I. Introduction 447
II. Methods of preparation 447
III. Physical properties 450
IV. Chemical properties 451
V. Possibilities for the practical application of organosilathianes 456

I. INTRODUCTION

The methods of synthesis and the physical and chemical properties of organosilathianes, and the possibility of their practical application, have been the subject of a large number of papers, which have not yet been reviewed. The increasing use of organosilathianes in polymer chemistry and in preparative synthesis, and the accumulation of experimental data on their methods of synthesis and properties, make it necessary to systematise the available material. The present review examines published work on the synthesis, properties, and applications of organosilathianes, published up to 1986.

II. METHODS OF PREPARATION

1. The Reaction of Organosilicon Compounds with Sulphur

A simple and convenient method for obtaining organosilathianes is by the insertion of sulphur at an Si–H bond.[1-5] The resulting organosilane thiols, when left to stand,[6] heated,[5] or treated with organochlorosilanes[7,8] or organoaminosilanes,[9] are converted into organosilathianes:

$$2Ar_nR_{3-n}Si{-}H + S \xrightarrow[\text{decalin, } 10\text{-}20\text{ h}]{180\text{-}200^\circ} 2Ar_nR_{3-n}SiSH \xrightarrow{-H_2S} (Ar_nR_{3-n}Si)_2S \quad (1)$$

$Ar = Ph$; $R = Me, Et, Pr, Ph$

$$3Ph_2SiH_2 + 6S \xrightarrow{-3H_2S} (Ph_2SiS)_3$$

$$4PhSiH_3 + 12S \xrightarrow{-6H_2S} PhSi(SSiPh)(SSiPh)(SSiPh)$$

$$R_3SiSH + ClSiR'_3 + R''_3N \xrightarrow[-R''_3N\cdot HCl]{} R_3SiSSiR'_3 \quad (2)$$

$$(RO)_3SiSH \xrightarrow{(R'O)_3SiNH_2,\ -(RO)_3SiSiNH_4} (RO)_3SiSSi(OR')_3$$

$$(RO)_3SiSH \xrightarrow{Me_3SiNR''_2,\ -(RO)_3SiSH_4NR''_2} (RO)_3SiSSiMe_3$$

$NR''_2 = NEt_2$, $NHSiMe_3$.

In reaction (2), instead of organosilane thiols, it is possible to use alkali and alkaline earth metal triorganosilanethiolates:[2,10]

$$(R_3SiS)_nM + nClSiR'_3 \rightarrow nR_3SiSSiR'_3 + MCl_n$$

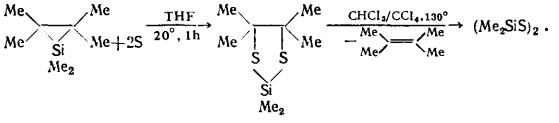
$M = Li, Na, K$ $(n=1)$ [2]; Ca, Sr, Ba $(n=2)$ [10] .

At a high temperature, sulphur is also inserted into the Si–C bond. For example, tetrabutylsilane at 240° gives hexabutyldisilathiane:[11]

$$Bu_4Si + S \rightarrow [Bu_3SiSBu] \rightarrow (Bu_3Si)_2S + Bu_2S \ .$$

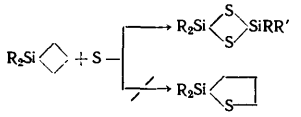
A similar reaction is observed with disilylhydronaphthalenes.[12]

The introduction of sulphur into strained silicon-containing rings takes place under much milder conditions (20°, 1–3 h), for example:[13]



With increase in temperature, the insertion product decomposes to a cyclic silathiane and an unsaturated hydrocarbon.

Cyclosilathianes are also obtained by the reaction of sulphur with dialkylsilacyclobutane[14] and with compounds containing Si–Si bonds:[15]



$$R_2HSiSiHR_2 + S \rightarrow (R_2SiS)_2 + R_2SiH_2 + R_3SiH + R_2Si(SSi(H)R)$$

$$R_3SiSiR_3 + S \rightarrow (R_2SiS)_2$$

$$(Me_2Si)_5 + S \xrightarrow{180^\circ} (Me_2Si)_5S$$

$R = Me$, i-Pr, t-Bu, cyclohexyl .

Sulphur is very easily inserted at an Si–Hg bond; the resulting unstable insertion product decomposes under the influence of ultraviolet radiation[16-18] or when heated:[19]

$$(Et_3Si)_2Hg + S \xrightarrow{20^\circ} Et_3SiSHgSiEt_3 \rightarrow (Et_3Si)_2S + Hg$$

$$(Et_3SiS)_2Hg \xrightarrow{\Delta} (Et_3Si)_2S + HgS \ .$$

Finally, sulphur can be inserted directly at an Si–S bond, forming organosilylsulphanes:[20]

$$R_3SiSSiR_3 + nS \xrightarrow{200^\circ} R_3SiS_{n+1}SiR_3$$

$R = Me, Et$; $n = 1-8$.

2. Reactions with Hydrogen Sulphide

The most widely used method for synthesising organosilathianes is by the thiolysis of organochlorosilanes in a solvent in the presence of tertiary amines. This method was used to obtain the first linear[21–23] and cyclic[24–26] silathianes:

$$2R_3SiCl + H_2S + 2R'_3N \xrightarrow[-2R'_3N\cdot HCl]{} (R_3Si)_2S \ .$$

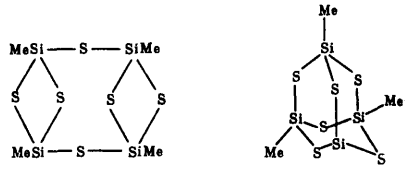
With triorganohalogenosilanes, this reaction gives hexaorganodisilathianes:[21,22,27–32] when the silicon atom has a substituent with a high electronegativity or a large volume, triorganosilane thiols are obtained in addition to disilathianes. The conversion of silane thiols or their salts to disilathianes is readily carried out by reactions (1)–(3).

The reaction of diorganodihalogenosilanes with hydrogen sulphide gives cyclic silathianes:[33–36]

$$nR_2SiCl_2 + nH_2S \xrightarrow[-2nR_3N\cdot HCl]{2nR_3N} (R_2SiS)_n \ . \quad (4)$$
$$n = 2, 3$$

With methyldichlorosilane, the reaction products, in addition to trimethylcyclotrisilathiane, also contain crystalline $[(MeSi)_2S_3]_2$,[33] which is assigned the structure (I)[31] or (II):[34,38]

$$MeHSiCl_2 + H_2S \xrightarrow[-R_3N\ HCl]{R_3N} (MeHSiS)_3 + \left[(MeSi)_2S_3\right]_2$$



(I)

(II)

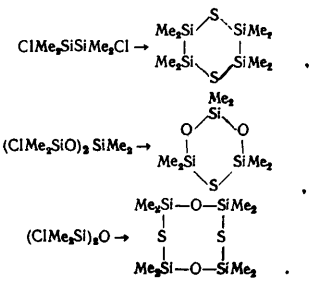
Products of this type are obtained by the reaction of H_2S with methyl(methoxy)dichlorosilane or organotrichlorosilanes in the presence of a hydrogen chloride acceptor:[24,31,37,39]

$$RSiCl_3 + H_2S \xrightarrow[-R_3N\cdot HCl]{R_3N} [(RSi)_2S_3]_2 \xleftarrow[-MeOH]{R_3N,\ -R_3N\cdot HCl} Me(MeO)SiCl_2 + H_2S \ .$$

With a deficit of the tertiary amine, 1,3-dichloro-1-3-dialkylcyclodisilathianes (III) can be isolated from the reaction mixture;[24] compounds (III) react further with hydrogen sulphide and the amine to give $[(RSi)_2S_3]_2$, confirming structure (I):

$$2PrSiCl_3 + 2H_2S + 4C_5H_5N \rightarrow \underset{\text{(IiI)}}{\text{Pr(Cl)Si(S)(S)Si(Cl)Pr}} \xrightarrow{2H_2S,\ 4C_5H_5N} (I) \ .$$

Various organochlorosilanes and organosiloxanes also undergo thiolysis and cothiolysis. This makes it possible to obtain a wide range of cyclic products,[40–43] for example:



The reaction of triethyl- and tripropylsilylamines and triethyl-N-(2-phenylethyl)silylamine with hydrogen sulphide gives the disilathiane and a small quantity of the silane thiol:[21,44]

$$Et_3SiNH_2 + H_2S \rightarrow (Et_3Si)_2S + Et_3SiSH \ .$$

Tris-silylamine and N-methyldisilylamine absorb H_2S at room temperature and under pressure to give disilathianes and ammonium salts of silane thiols:[45,46]

$$(H_3Si)_3N + 2H_2S \rightarrow H_3SiS^-NH_4^+ + (H_3Si)_2S$$
$$(H_3Si)_3NMe + 3H_2S \rightarrow (H_3Si)_2S + 2H_3SiS^-MeNH_3^+ \ .$$

Treatment of these salts with trimethylchlorosilane gives unsymmetrical trimethyldisilathiane,[45] and the reaction with BCl_3 gives disilyl sulphide:[46]

$$H_3SiSH\cdot NH_3 + Me_3SiCl \xrightarrow{-NH_4Cl} H_3SiSSiMe_3$$
$$H_3SiSH\cdot MeNH_2 + BCl_3 \xrightarrow[-MeNH_3\cdot HCl]{} [(H_3SiS)_3B] \xrightarrow[-B_2S_3]{} (H_3Si)_2S \ .$$

Hexamethyldisilazane and N-trimethylsilylaniline reacts with hydrogen sulphide with difficulty to give trimethylsilanethiol in ~14% yield.[45]

At the boiling point, organocyclosilazanes undergo slow thiolysis with the subsequent transformation of the silazane groups into silathiane groups:[47,48]

$$[R_2SiNH]_n \xrightarrow[-NH_4SH]{2nH_2S} \left[(R_2SiNH)_{n-1}(R_2SiS)\right] \xrightarrow[-NH_4SH]{2nH_2S} \left[(R_2SiNH)_{n-2}(R_2SiS)_2\right] \longrightarrow \cdots \rightarrow$$
$$\xrightarrow[-(n-2)NH_4SH]{2(n-2)H_2S} [R_2SiS]_m \quad (5)$$
$$R = Alk,\ m = 2, 3;\ n = 3, 4 \ .$$

Imidazole is an effective catalyst for the thiolysis of hexamethyldisilazane.[49–51] Its catalytic action involves the ready formation of N-trimethylsilylimidazole, which subsequently silylates hydrogen sulphide:[51]

$$(Me_3Si)_2NH + 2HN\langle\rangle \xrightarrow{-NH_3} 2Me_3SiN\langle\rangle \xrightarrow[-2HN\langle\rangle]{H_2S} (Me_3Si)_2S \ .$$

Another method of improving reaction (5) is by the combined thiolysis of SiN- and SiCl-containing compounds:[52,53]

$$2(Me_3Si)_2NH + 3H_2S + 2Me_3SiCl \rightarrow 3(Me_3Si)_2S + 2NH_4Cl \ , \quad (6)$$

$$(R_2SiNH)_n + R_2SiCl_2 + H_2S \xrightarrow{-NH_4Cl} (R_2SiS)_m \ , \quad (7)$$
$$n = 3, 4;\ m = 2, 3$$

$$Me_3SiNR_2 + H_2S + Me_3SiCl \rightarrow (Me_3Si)_2S + R_2NH\cdot HCl \ . \quad (8)$$

Carboxylic acid silylamides[54] and trimethylcyanosilane[55] react readily with hydrogen sulphide to give hexamethyldisilathiane in high yield (86%):

$$\left.\begin{array}{l} MeC(OSiMe_3)=NSiMe_3 \xrightarrow[-MeCONHSiMe_3]{H_2S} \\ Me_3SiCN \xrightarrow[-HCN]{H_2S} \end{array}\right\} \rightarrow (Me_3Si)_2S \ .$$

To conclude this section, mention must be made of a method for obtaining disilathiane by the action of an electric discharge on an equimolar mixture of SiH_4 and H_2S.[56]

3. Reactions of Hexamethyldisilathiane

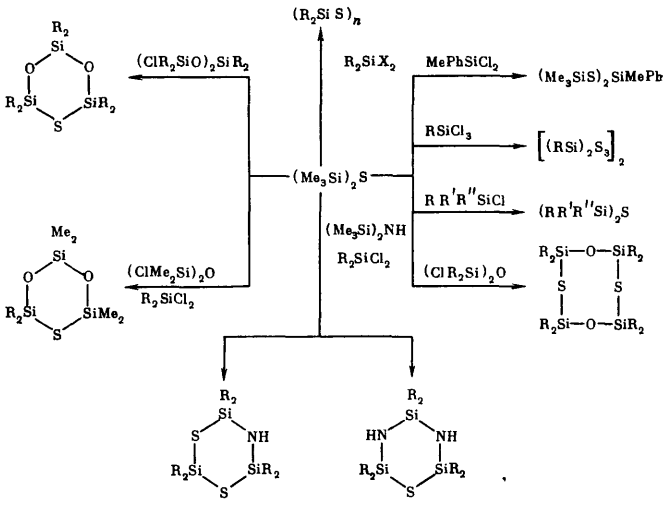
Reactions (6) and (8) have proved extremely promising for the synthesis of linear organosilathianes, in particular hexamethyldisilathiane, which has been obtained chromatographically pure in almost quantitative yield. The synthesis of cyclic silathianes by reaction (7), however, in spite of the high activity of the starting materials, has a significant disadvantage, namely the formation in a number of cases of a mixture of cyclosilathianes and cyclosilathiazanes, difficult to separate.

An effective method for the synthesis of linear and cyclic organosilathianes, organosilathiaoxanes, and organosilathiazanes is based on the trans-silylation of hexamethyldisilathiane by organochlorosilanes:[57]

$$n/2\ (Me_3Si)_2S + R_{n-4}SiCl_n \rightleftarrows nMe_3SiCl + R_{4-n}SiS_{n/2} \quad (9)$$
$$R = Alk, Ar;\ n = 1-3$$

This equilibrium reaction takes place with difficulty even on prolonged heating (200–250 °C). In the presence of catalytic quantities of amines or DMF, however, its rate increases markedly, and the reaction is quantitative when the trimethylchlorosilane is continuously removed.

The extensive synthetic possibilities of reaction (9) can be illustrated by the following examples:[57–62]



These examples show that this method can be used to obtain organosilicon compounds containing Si–S–Si bonds with practically any specified structure.

The splitting of cyclosilathianes by bifunctional organosilanes has been proposed as a method of obtaining polymeric organosilathianes.[63] An NMR study of the equilibrium of the reaction between $(Me_2SiS)_3$ and Me_2SiX_2, where X = Cl, Br, OMe, SMe, at 150 °C and 200 °C showed that the reaction is displaced towards the formation of the cyclic dimers and trimers, and also short chain molecules.[64,65]

4. Reaction with Inorganic Sulphides

A general method for synthesising organosilathianes is by the reaction of organo-iodosilanes with the sulphides of silver[23,24,66–68] and mercury:[68–77]

$$2nR_3SiI + M_nS \rightarrow (R_3Si)_2S + MI_n$$
$$R = Alk, Ar;\ M = Hg, Ag;\ n = 1, 2$$

The same reaction can be used to obtain Si–H-containing organosilathianes:[76,77]

$$Me_nH_{3-n}SiI + HgS \xrightarrow[-HgI]{35^\circ} (Me_nH_{3-n}Si)_2S$$

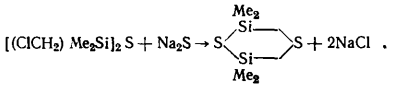
The reaction of mercury sulphide with di-iodosilane gives a mixture of oligomers $(H_2SiS)_x$, containing as the principal component $(H_2SiS)_3$, which cannot be isolated from the mixture, because of its low thermal stability. When kept in the light (20°, 8 d), the oligomers are converted into a resinous polymer, which when heated in a vacuum is depolymerised to give trisilathiane. Unlike its alkyl homologues, trisilathiane is unstable, and polymerises at room temperature. In contact with pumice or aluminium sulphide, its stability is increased, and decomposition begins only at 250 °C:[77]

$$HgS + H_2SiI_2 \xrightarrow[benzene]{80^\circ} (H_2SiS)_n \xrightarrow[10^{-3}\ mmHg]{210^\circ} (H_2SiS)_3 \xrightarrow[[Al_2S_3]]{250^\circ} H_3SiSH + (H_3Si)_2S + H_2S$$

The passage of trimethylchlorosilane vapour (400°) through a molten eutectic LiCl/KCl mixture containing 25% potassium sulphide gave hexamethyldisilathiane in 81% yield.[78,79]

Hexamethyldisilathiane is also formed when trimethylchlorosilane is heated with anhydrous sodium sulphide in a sealed tube.[80]

Sodium sulphide can also be used to obtain cyclic silathianes, for example:[81]

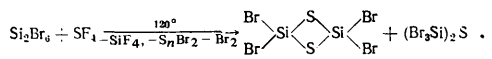


Organochlorosilanes react vigorously with ammonium hydrogen sulphide even in the cold, to give organosilathianes in high yield (up to 90%):[82]

$$2R_3SiCl + 2NH_4SH \xrightarrow[-H_2S]{-2NH_4Cl,} (R_3Si)_2S$$

In addition to the desired compounds, the reaction products also include Si–N-containing compounds, formed by an ammonolysis side reaction.

The reaction of disilanes with sulphur tetrafluoride can in principle be used to synthesise various organosilathianes:[83]



Hexamethyldisilathiane has been isolated as one of the products of the reaction of trimethyl(dimethylamino)silane with phosphorus pentasulphide:[84]

$$8Me_3SiNMe_2 + P_4S_{10} \rightarrow 2\ (Me_3Si)_2S + 4\ (Me_2N)_2P(S)SSiMe_3$$

5. Thermal Rearrangements of Sulphur-Containing Organosilicon Compounds

When distilled at atmospheric pressure, hexamethylcyclotrisilathiane undergoes rearrangement to give the cyclic dimer:[36,64,85]

$$2(Me_2SiS)_3 \rightleftarrows 3(Me_2SiS)_2 \quad (10)$$

A ^1H NMR study of this equilibrium in solution showed that high temperatures and high dilution facilitate the formation of small rings. The ring strain energy in the cyclic dimer is ~3 kcal per monomer unit.[86]

2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilathiane[36] and hexaphenylcyclotrisilathiane[35] behave similarly.

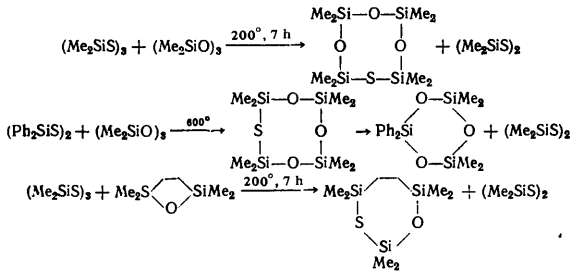
The existence of equilibrium (10) explains the lack of agreement in the physical constants given by many authors for various cyclosilathianes. For example, for hexaphenylcyclotrisilathiane, melting points 188–198° [35] and 191–193° [4] have been given; two melting points have also been given for trimethyltriphenylcyclotrisilathiane: 109° [59] and 112.5–114°.[87] It has been suggested that reaction (10) may take place with the intermediate formtion of silathiane oligomers[64,65,67] or the unstable species $[R_2Si=S]$:[88]

$$(Me_2SiS)_3 \rightleftarrows -(-Me_2SiS-)_n- \rightleftarrows (Me_2SiS)_2 \quad (11)$$

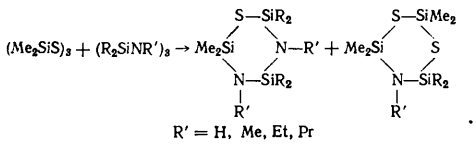
$$(Me_2SiS)_3 \rightleftarrows [Me_2Si=S] + (Me_2SiS)_2$$
$$2[Me_2Si=S] \rightleftarrows (Me_2SiS)_2 \quad (12)$$

Equilibrium (11) was proved in Refs.63, 65, and 77, and reaction (12) was confirmed by carrying out the reactions of cyclosilathianes with hexamethylcyclotrisiloxane or 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane, which act as "traps" for $[Me_2Si=S]$. Thus when

these reagents are heated, the products are the cyclosilathiaoxanes and the cyclodisilathiane:[88-90]

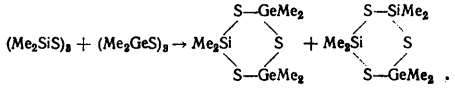


Cyclic organosilathiazanes have been obtained by heating hexamethylcyclotrisilathiane and hexaorganocyclotrisilazanes:[91,92]



Depending on the group, this exchange reaction gives a mixture of the cyclotrisiladithiazane and the cyclotrisilathiadiazane or only the cyclotrisiladithiazane.

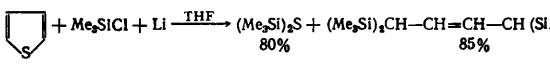
The exchange reaction between hexamethylcyclotrisilathiane and hexamethylcyclotrigermanium sulphide gives mixed heterocyclic compounds containing silicon, germanium, and sulphur atoms:[93]



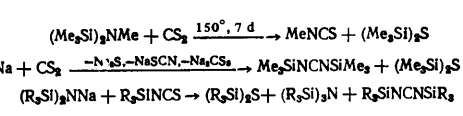
6. Other Methods

This section deals with studies whose aim was not the directed synthesis of organosilathianes.

An exception is the reaction of thiophene with the reagents usually employed for C-silylation:[94]

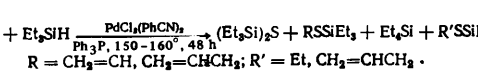


Silazanes and their N-metal derivatives react with CS_2, COS, and RNCS to give mixtures of products including hexamethyldisilathiane:[92-98]

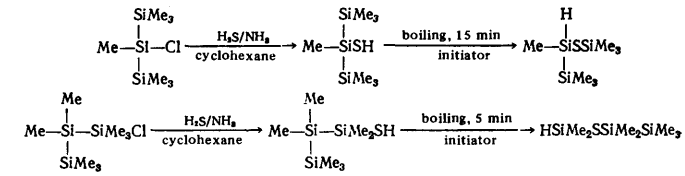


A similar result was obtained in the reaction of carbon disulphide with trimethylsilyl esters of isothiocyanatocarboxylic acids.[99]

The splitting of unsaturated sulphides by triethylsilane, in addition to other products, gives hexaethyldisilathiane:[100]

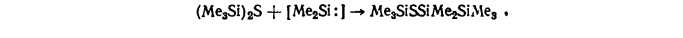


Under the influence of the radical reaction initiators benzoyl peroxide or azo-bis-isobutyronitrile, trisilanethiols undergo rearrangement to give silathianes:[101]

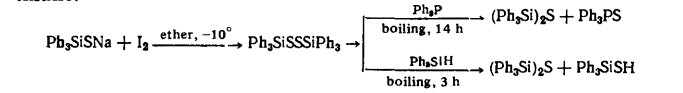


Trialkylsilanethiols do not undergo this rearrangement, even on prolonged boiling in xylene.

The insertion of dimethylsilylene, obtained by the thermal decomposition of $(Me_2Si)_6$, at an Si–S bond provides an interesting method for obtaining unsymmetrical silathianes:[102]



Hexaphenyldisilyl disulphide is obtained by the action of iodine on sodium triphenylsilanethiolate.[103] Treatment of this compound with triphenylphosphine or triphenylsilane gives hexaphenyldisilathiane:



III. PHYSICAL PROPERTIES

In spite of recent progress in the synthesis of organosilathianes, their physical properties have been comparatively little studied.

Data on the structure of various linear and cyclic organosilathianes have been obtained by electron diffraction and microwave spectroscopy:[104,105]

Compound	Bond length Si–S, Å	Si–S–Si	Angles, degrees S–Si–S	Refs.
$(Me_2SiS)_2$	2.18±0.03	75	105	[104, 105]
$(Me_2SiS)_3$	2.15±0.03	110	115	[104, 105]
$(H_3Si)_2S$	2.136±0.002	97.4±0.7	—	[6]

Comparison with the C–S–C angle in dimethyl sulphide (98°51′)[106] shows that there is no π-bonding in disilyl sulphide.

The Si–S–Si stretching bands in the infrared (IR) spectra of linear and cyclic silathianes lie in the following ranges (cm^{-1}):[107] 396–416 $[(Cl_3Si)_2S]$; 437–493 $[(Me_3Si)_2]$; 480–524 $[(H_3Si)_2S]$; 493–530 $\{[(PhCH_2)_3Si]_2S\}$; 519–556 $\{[(p\text{-}MeC_6H_4)_3Si]_2S\}$; 518–572 $[(Ph_3Si)_2S]$. The displacement of ν_{Si-S} to higher wavenumbers is attributed to the decrease in the polarity of this bond in the last three compounds. It has been suggested[107] that in view of the strong inductive effect of the phenyl group, structures $Ph_3Si^- = S^+$ with a $(p \rightarrow d)_\pi$ double bond plays a significant part in the resonance system.

The Raman and IR spectra of hexamethyldisilathiane have been used to determine the force constant (2.20×10^5 dyne cm^{-1}), The Si–S–Si angle (104°), and the bond dissociation energy (63 kcal $mole^{-1}$).[108]

An overall similarity is observed in the Raman spectra of hexamethyl- and hexachlorodisilathianes, whose molecules have C_{2v} symmetry. The comparatively small splitting of $\nu_{Si-S-Si}$ [47 cm^{-1} in $(Me_3Si)_2$ and 21 cm^{-1} in $(Cl_3Si)_2S$] shows that the Si–S–Si angle is close to 90°. The spectra of $(Me_2SiS)_2$ and $(Cl_2SiS)_2$ indicated that the Si_2S_2 ring is planar. On going from the linear to the cyclic disilathiane, the spectra show an increase in $\nu_{s(Si-S-Si)}$ and an increase in ν_{as} to approximately the same extent as on going from propane to cyclobutane.[109]

In the Raman spectrum of molten tetramethylcyclodisilathiane, the strongest lines of hexamethylcyclotrisilathiane were detected, indicating the existence of the equilibrium $3(Me_2SiS)_2 \leftrightarrows 2(Me_2SiS)_3$.[110]

The vibrational spectra indicate that $(Me_2SiS)_2$ has a planar structure with D_{2h} symmetry, in agreement with electron diffraction data and dipole moment measurements. The choice between models with symmetry C_{3v} (chair form) and C_s (boat form) for $(Me_2SiS)_3$ is not so obvious, although the combined spectroscopic data provide evidence for the latter. Comparison of data on the structure of cyclosilathianes with the magnitude of the Si−S−Si angle in $(H_3Si)_2S$ shows that the tetramethylcyclodisilathiane ring is strained as a result of a deviation from the normal valence angles.[110]

There are no unambiguous published data on the conformational transformations of cyclosilathianes. Thus according to X-ray diffraction data, *trans*-2,4,6-trimethyl-2,4,6-triphenylcyclotrisilathiane is present in the crystals in a boat form,[111] whereas in solution (according to ^1H NMR data) is is present as boat forms undergoing rapid interconversion, although the chair form cannot be completely excluded.[87]

Gas-phase electron diffraction showed that hexamethylcyclotrisilathiane is non-planar.[105] From a comparison of the experimentally determined value of the dipole moment with the values calculated for the chair and boat models, it was suggested[112] that $(Me_2SiS)_3$ exists chiefly in the chair form, although a small concentration of the boat form is possible. From the Raman and IR spectra, it was concluded[110] that hexamethylcyclotrisilathiane in the liquid state is present in the boat form.

The conformational transformations of methylphenyl-,[113] methylethyl-,[111] and methylvinylcyclosilathianes[111] have also been studied.

The dispole moment of hexamethyldisilathiane, measured in benzene at 25 °C, is 1.44 D. The dipole moments of $(Me_3Si)_2S$ and $(Me_3Si)_2O$ have been used to estimate the angles Si−S−Si (~97−98°) and Si−O−Si (~150°). The large difference in the angles is regarded as proof of $(p \rightarrow d)_\pi$ interaction in the Si−O bonds, and its absence in the Si−S bonds.[29]

The dipole moments of $(Me_2SiS)_2$ and $(Me_2SiS)_3$ have been calculated, assuming that the atomic polarisation of the cyclosilathianes is the same as that for the corresponding cyclosiloxanes: $\mu_{(Me_2SiS)_2}$ = 0.00; $\mu_{(Me_2SiS)_3}$ = 1.03 D.[112]

A study of compounds containing Si−S and S−Si−N bonds showed that the replacement of a C−S bond by an Si−S bond has no effect on the magnitude of the diamagnetic susceptibility;[114] similar data were obtained in Ref.115. This indicates that there is no $(p \rightarrow d)_\pi$ interaction in the Si−S bond.

Table 1. Effect of $(p \rightarrow d)_\pi$ conjugation in Si−E bonds.[40]

Physical properties	E = N		E = O		E = S	
	found	calculated	found	calculated	found	calculated
Bond length, Å	1.74±0.02; 1.72±0.03	1.81	1.63±0.04; 1.69±0.03	1.76	2.14±0.02	2.15
Force constant, mdyne Å^{-1}	4.1	3.3	4.7	3.7	2.2	2.2
Angle Si-E-Si, °	119.6±1; 131	109°28′	130±10; 145	109°28′	97.4±0.7; 104; 110	109°28′

The absence of this interaction is also indicated by ultraviolet (UV),[116] ^1H, ^{13}C,[117,118] and ^{29}Si NMR,[77] and Raman[119] spectroscopy.

Thus almost all studies of the physical properties of organosilathianes in one way or another deal with the problem of $(p \rightarrow d)_\pi$ conjugation. This problem is of primary importance for the chemistry of compounds containing Si−O and Si−N bonds, but it is not so important for the chemistry of organosilathianes, since the question of the existence of $(p \rightarrow d)_\pi$ conjugation in the Si−S−Si system has not yet been resolved unambiguously.

Thus from a comparison of the bond lengths, force constants, and Si−E−Si angles, it has been concluded that there is no $(p \rightarrow d)_\pi$ interaction in silathianes[40] (Table 1). This is confirmed by the physical properties of disilathianes.[6,120,121]

Nevertheless, many attempts have been made to estimate the extent of $(p \rightarrow d)_\pi$ conjugation in organosilathianes by UV, IR, and ^1H NMR spectroscopic studies.[122-131] It was assumed that $(p \rightarrow d)_\pi$ conjugation involves partial displacement of the p_π electrons of the S atom to the d_π orbitals of Si. As a result, the negative charge on the sulphur atom and the basic strength of the compound decrease.[129]

From an analysis of the IR spectra of substituted silicon hydrides containing Si−O and Si−S fragments, it was concluded[130] that the extent of $(p \rightarrow d)_\pi$ conjugation changes in the approximate ratio SiO : SiS = 2 : 1.

Thus $(p \rightarrow d)_\pi$ interaction (whether it exists or not) does not have the significant influence on the chemical properties of organosilathianes observed for organosiloxanes or organosilazanes. This is confirmed by a calculation of the overlap integrals of the Si−S bond,[131] where it was shown that the small magnitude of the overlap integral of the unoccupied atomic orbitals at this bond is one of the principal reasons for its high chemical activity.

IV. CHEMICAL PROPERTIES

An analysis of published data has shown that reactions involving the heterolytic splitting of Si−S−Si bonds in organosilathianes can be divided into two groups: exchange reations and insertion reactions.

The first group includes the great majority of known reactions of organisilathianes, taking place according to the general scheme:

$$\equiv Si-S-Si\equiv + X-Y \rightarrow \equiv Si-X + Y-S \ .$$

1) Y = H—"protic silylation" reactions (exchange between a silyl group and a mobile hydrogen atom), for example:

$$\equiv Si-S-Si\equiv + 2REH \rightarrow 2 \equiv SiER + H_2S. \qquad (13)$$

E = O, NH, S; R represents an organic or hetero-organic group.

2) Y = M—"aprotic silylation" reactions (exchange between a silyl group and a metal atom), for example:

$$\equiv Si-S-Si\equiv + HgR_2 \rightarrow 2\equiv SiR + HgS \ .$$

3) Y = Si—trans-silylation reactions (exchange between one silyl group and another), for example:

$$\equiv Si-S-Si\equiv + 2\equiv Si^*-E \rightleftarrows \equiv Si-S-Si^*\equiv + \equiv Si-E + \equiv Si^*-E \rightleftarrows \rightleftarrows \equiv Si^*-S-Si^*\equiv + 2\equiv Si-E \ .$$

4) Y = E—reactions involving the redistribution of functional groups (exchange between a silyl group and functional groups), for example:

$$X = Cl,\ \equiv Si-S-Si\equiv + 2\rangle P-Cl \rightarrow 2\equiv Si-Cl + \rangle P-S-P\langle$$

$$X = O,\ \equiv Si-S-Si\equiv + \equiv Sn-O- \rightarrow 2\equiv Si-O- + \equiv Sn-S- \ .$$

The second group includes reactions taking place according to the

$$\equiv Si-S-Si\equiv + X-Y \rightarrow \equiv Si-S-X-Y-Si\equiv \ . \qquad (14)$$

1) 1,1-insertion, for example:

$$\equiv Si-S-Si\equiv + [:SiR_2] \rightarrow \equiv Si-S-SiR_2-Si\equiv \ .$$

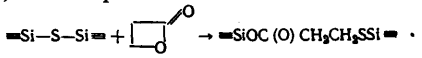
2) 1,2-insertion, for example:

$$\equiv Si-S-Si\equiv + (CF_3)_2CO \rightarrow \equiv SiOC(CF_3)_2S(CF_3)_2COSi\equiv .$$

3) 1,3-insertion, for example:

$$\equiv Si-S-Si\equiv + CH_2(O)CH_2 \rightarrow \equiv SiOCH_2CH_2SCH_2CH_2OSi\equiv ,$$

4) 1,4-insertion, for example:



5) 1,*n*-insertion, or example:

$$\equiv Si-S-Si\equiv + S_8 \rightarrow \equiv Si-S_n-Si\equiv .$$

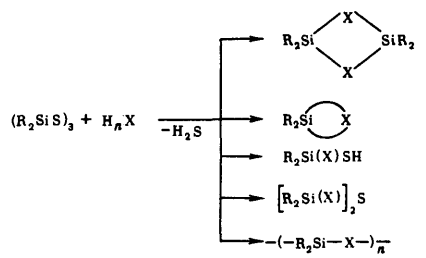
1. Exchange Reactions

a) "Protic silylation"

The reaction of organosilathianes with proton-donor reagents involves exchange between a mobile proton of an inorganic, organic, or hetero-organic compound and a silyl group.[62] Organosilathianes silylate monohydric and polyhydric alcohols and phenols,[30,80,132–144] aminoalcohols and phosphorylated alcohols,[139,145] mineral and carboxylic acids,[70,71,90,146,149] inorganic and organic acids of phosphorus,[61,146,150,151] boron, arsenic, and sulphur,[61,151] enols,[152] aldoximes and ketoximes,[152] aromatic thiols, thioglycols,[61,153] amines and their derivatives,[80,154] and silanols and siloxanediols;[155] the silyl derivatives are formed in high yields.

Depending on the original reagent ratio, products of complete or partial silylation may be formed. In the case of cyclic silathianes, monomeric linear and cyclic compounds, and also polymers, have been obtained:

$$(R_3Si)_2S + 2H^{\pm}_nX \xrightarrow{-H_2S} 2R_3SiXH_{n-1} \rightarrow \cdots \rightarrow \xrightarrow[-H_2S]{(R_3Si)_2S} (R_3Si)_nX$$



The following general regular features of this reaction (13) have been established: the presence of bulky or electron-donor substituents on the silicon atom leads to a decrease in the activity of organosilathianes. The introduction of alkoxy groups into the silathiane molecule leads to the same result, and this has been attributed[135,137] to an increase in the $(p \rightarrow d)_\pi$ interaction in the Si–S bond. Cyclic silathianes are more active than the linear compounds, and cyclodisilathianes have the highest activity.[135,137]

A study of the model reaction of hexamethyldisilathiane with various proton donors (REH) made it possible to arrange them in the following order of decreasing activity: ROH > RR^1NH > RSH. This order corresponds to the decrease in the energy of the ≡Si–E bond formed in reaction (13).[61] The rate of the reaction of organosilathianes with proton donors increases when the molecule of the proton donor contains electron-acceptor substituents, which increase its acidity, and also when the reaction is carried out in polar solvents and in the presence of nucleophilic catalysts (tertiary amines, DMF, acetonitrile).[61]

The synthetic possibilities provided by organosilathianes as silylating reagents have been demonstrated by the reactions of hexamethyldisilathiane and hexamethylcyclotrisilathiane with a wide range of proton donors (Tables 2 and 3).

b) Aprotic silylation

There are only a few published examples of silathiane reactions of this type: the splitting of Si–S–Si bonds by organic compounds of mercury[156–162] and phenyl-lithium.[2]

Depending on the organic group, organomercury compounds react with organosilathianes to give products containing an Si–C or an Si–O bond:

$$(Me_3Si)_2S \xrightarrow{-HgS} \begin{cases} \xrightarrow{Hg(CONEt_2)_2} Me_3SiCONEt_2 \\ \xrightarrow{Hg(COOMe)_2} Me_3SiOMe + Me_3SiCOOMe \\ \xrightarrow{Hg[C(N_2)COOEt]_2} Me_3SiCN_2COOEt \\ \xrightarrow{Hg(CH_2COOR)_2} Me_3SiCH_2COOR , \end{cases} \quad (15)$$

$$R_3SiSSiMe_3 \xrightarrow{-HgS} \begin{cases} \xrightarrow{Hg(CH_2COR')_2} R_3SiOC(R')=CH_2 + Me_3SiCH_2COR' \\ \xrightarrow{HgR''_2} R_3SiR'' + R''SiMe_3 , \end{cases} \quad (16)$$

$$(R_3Si)_2S + Hg(CH_2COR'')_2 \rightarrow 2R_3SiOC(R'')=CH_2 + HgS \quad (17)$$

R_3=MePhC$_{10}$H$_7$-α; R′=H, Me, OMe, Ph; R″=MeCOO, MeO; R‴=OMe, OCH=CH$_2$, OCOPh, OCOMe

Reactions (15)–(17) provide an effective method for synthesising a number of silicon compounds which are difficult to obtain; in particular, a new class of compound, carbamoylsilanes, has been synthesised in this way.[158]

In the reaction of phenyl-lithium with hexaphenyldisiladithiane, the S–S bond, and not the Si–S bond, is split first:[2]

$$Ph_3SiS-SSiPh_3 + PhLi \rightarrow Ph_3SiSLi + PhSSiPh_3 \xrightarrow[-PhSLi]{PhLi} Ph_4Si .$$

c) Trans-silylation reactions

The principal regular features and synthetic possibilities of the trans-silylation of organosilathianes by organohalogeno- and organopseudohalogenosilanes and -siloxanes were discussed in section II.

d) Reactions involving the redistribution of functional groups

Organosilathianes are split by inorganic halides to give the corresponding sulphides and organohalogenosilanes

$$\equiv Si-S-Si\equiv + M-X \rightarrow 2\equiv Si-X + M-S \quad (18)$$

MX=BCl_3 [153], PCl_3, PBr_3, $POCl_3$ [163]; PCl_5 [164]; $AsCl_3$, $SbCl_3$ [165]; $TiCl_4$ [166, 167]; $SnCl_4$, VCl_3, $CrCl_3$ [167]; $PdCl_2$ [166]; $HgCl_2$ [70]; $PbCl_2$, $CdCl_2$, AgCl, AgBr [23]; NH_4Cl, KBr [168]; HgI_2 [169]

The splitting of the Si–S bond by the ammonium, sodium, and potassium salts of inorganic and organic acids[168] and by silver salts (AgCN, AgNCS, AgNCO, AgOCOMe) [23] takes place similarly. Hexa-alkyldisilathianes do not react with silver iodide.[23]

Disilathiane[70] and 1,3-dimethyldisilathiane[71] do not react with methyl iodide, and hexamethyldisilathiane does not react with lower alkyl halides.[61] On prolonged boiling, higher alkyl halides react with organosilathianes according to the scheme:

$$\equiv Si-S-Si\equiv \xrightarrow[-\equiv SiX]{RX} \equiv SiSR \xrightarrow[-\equiv SiX]{RX} R_2S .$$

Table 2. Reactions of hexamethyldisilathiane with proton donors REH.

REH	Reagent ratio REH : $(Me_3Si)_2S$	Reaction conditions	Products (yield, %)	Refs.
ROH	1:2	Δ	Me_3SiOR, R = Et (75), Bu (94), iso-Pr (78), t-Bu (58)	[80]
			$C_{12}H_{25}$ (87.5)	[139]
$HO(CH_2)_4OH$	1:1;	100–110°, 2 h	$Me_3SiO(CH_2)_4OSiMe_3$ (97.5)	[139]
	2:1	ditto	$Me_3SiO(CH_2)_4OH$ (55)	[139]
$EtC(CH_2OH)_3$	3:2	»	$EtC(CH_2OSiMe_3)_3$ (76.5)	[139]
$HOCH_2CH(OH)CH_2OH$	3:2	»	$Me_3SiOCH_2CH(OSiMe_3)CH_2OSiMe_3$ (96)	[139]
$HO(CH_2)_2NH_2$	1:2;	20°, 0.5 h	$Me_3SiO(CH_2)_2NH_2$ (98.5)	[139]
	1:1	100°, cat. C_5H_5N	$Me_3SiO(CH_2)_2NHSiMe_3$ (82.8)	[139]
$[HO(CH_2)_2]_2NH_2$	1:1;	20°, 0.5 h	$[Me_3SiO(CH_2)_2]_2NH$ (78.5)	[139]
	2:1	ditto	$Me_3SiO(CH_2)_2NH(CH_2)_2OH$ (44)	[139]
$[HO(CH_2)_2]_3N$	3:2;	»	$[Me_3SiO(CH_2)_2]_3N$ (73.2)	[139]
	1:1	»	$[Me_3SiO(CH_2)_2]_2N(CH_2)_2OH$ (91)	[139]
PhCH(OH)COOR	1:2	70–90°, 1–2 h	PhCH(OSiMe$_3$)COOR, R=Et (93), Pr (91)	[142]
$(RO)_2P(O)CR'R''(OH)$	1:2	50–70°, 0.5–1 h	$(RO)_2P(O)CR'R''(OSiMe_3)$, R=Me, R'=H; R''=Me (92), Ph (90); R'=Me, R''=Et (80); R=Et, R'=H, R''=Me (89), Ph (97)	[145]
$RCOCH_2COMe$	1:2	50—70°, *	$RCOCH{=}C(OSiMe_3)Me$, R=Me (78), Ph (92)	[152]
CH(R)C(O)CH_2C(O)CH(R) |——CH_2——|	1:2	ditto	CH(R)C(O)CH=C(OSiMe$_3$)CH(R), |——CH_2——| R=H (86), Me (80)	[152]
RR'C=NOH	1:2	50—70°	RR'C=NOSiMe$_3$; R=R'=Ph (95); R=H, R'=Me (85), Ph (89); R=Me, R'=Me (96), Ph (94)	[152]
XC_6H_4OH	1:2	80°, 1.5 h	$XC_6H_4OSiMe_3$, X=3-Me (74.3) 2-Me_3SiO (76.3); 2-OH (75.9); 3-Me_3SiO (72.4); 4-Me_3SiO (74.3); 2,3-$(Me_3SiO)_2$ (65.9); 3-NH_2 (96); 2-C_6H_5 (77.9); 4-MeCONH (73.8); 3-OH (76.1); 4-OH (43.1); 2.3-$(OH)_2$ (48.8)	[148]
$1,2,3\text{-}(HO)_3C_6H_3$	1:1	80°, 2.5 h, toluene	3-OH-1,2-$(Me_3SiO)_2C_6H_3$ (76.5)	[148]
Bu_2NH	1:2	boiling., 3 d	Bu_2NSiMe_3 (49)	[80]
RNH_2	1:2	boiling 25 h	$RNHSiMe_3$, R=Bu (13); R=Ph (85)	[80]
$PhNH_2$	1:2	100°, 2.5 h, cat. C_5H_5N	$PhNHSiMe_3$ (94.3)	[154]
$HOC_6H_4NH_2$	1:1	ditto	$Me_3SiOC_6H_4NHSiMe_3$ (79.2)	[154]
$H_2NCH_2CH_2NH_2$	1:1	»	$Me_3SiNHCH_2CH_2NHSiMe_3$ (85.2)	[154]
H_2SO_4	1:1	18–20°, 1 h	$(Me_3SiO)_2SO_2$ (92.5)	[147]
H_3PO_4	3:2	20°, 1 h	$(Me_3SiO)_3PO$ (95.6)	[146]
H_3PO_3	3:2	120°, 4 h	$(Me_3SiO)_3P$ (81.5)	[146]
$H_2S_2O_7$	1:1	—	$(Me_3SiOSO_2)_2O$ (74)	[149]
$XC_6H_4P(OH)_2$	1:2	40—80°	$XC_6H_4P(O)(OSiMe_3)H$, X=H (93), 4-Me (91)	[150]
$PhP(OH)_2$	1:1	ditto	$PhP(OSiMe_3)_2$ (75)	[150]
$PhB(OH)_2$	1:1	100° ditto	$PhB(OSiMe_3)_2$ (72)	[151]
$PhAs(O)(OH)_2$	1:1	»	$PhAs(O)(OSiMe_3)_2$ (54)	[151]
$PhSO_2OH$	1:2	»	$PhSO_2OSiMe_3$ (96)	[151]
$(RO)_2POH$	1:2	100–120°, 2–5 h	$(RO)_2POSiMe_3$, R=Me (81); Et (72), iso-Pr (84), Ph (84)	[151]
R_2POOH	1:2	40–60°, 0.5–2 h	$R_2POOSiMe_3$, R=Me (92), Et (89), Ph (73)	[151]
R_2PSOH	1:2	ditto	$R_2PSOSiMe_3$, R=Et (95), MeO (96), EtO (97)	[151]
$(RO)_2POOH$	1:2	»	$(RO)_2POOSiMe_3$, R=Me (93), Et (92)	[151]
$(RO)_2PSSH$	1:2	»	$(RO)_2PSSSiMe_3$, R=Me (94.5), Et (92), iso-Pr (89)	[151]
Ph_2PH	1:2	cat.	no reaction	[61]
RSH	1:2	boiling, 50 h	no reaction for R = Et, Bu, C_5H_{11}, C_2 = $=CHCH_3$ [61]	[61]
PhSH	1:2	100°, 0.5 h	$PhSSiMe_3$ (88)	[61]
MeCOOH	1:2	80°, 0.5 h	$MeCOOSiMe_3$ (88.3)	[146]
$CH_2{=}C(CH_3)COOH$	1:2	70—80°	$CH_2{=}C(CH_3)COOSiMe_3$ (87.9)	[146]
$(CH_2COOH)_2$	1:1	110–140°, 4 h	$(CH_2COOSiMe_3)_2$ (98.7)	[146]
$(CH_2CH_2COOH)_2$	1:1	50–60°, 2 h	$(CH_2CH_2COOSiMe_3)_2$ (55.2)	[146]
HOC_6H_4COOH	1:1	80–90°, 1 h	$Me_3SiOC_6H_4COOSiMe_3$ (80)	[146]
$Ph_2Si(OH)_2$	1:1	120–125°, 0.5 h, cat. $(Me_3SiO)_2POH$	$Ph_2Si(OSiMe_3)_2$ (83)	[155]
$HOSiMe_2OSiMe_2OH$	1:1	90–95°, 0.5 h, cat. $(Me_3SiO)_2POH$	$Me_3SiOSiMe_2OSiMe_2OSiMe_3$ (95)	[155]

*Boiling until liberation of H_2S stopped.

Increase in the electron-acceptor power of the substituents on the carbon atom of the alkyl halide, the polarity of the medium, and the basic strength of the sulphur atom increases the reactivity of organosilathianes towards alkyl halides.[61]

Acyl halides are much more reactive than alkyl halides towards organosilathianes:[61,170–172]

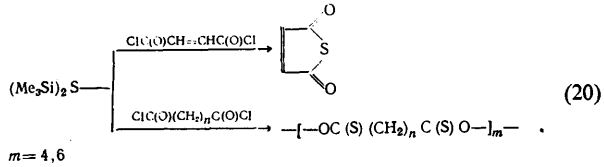
$$\equiv Si{-}S{-}Si \equiv \xrightarrow[-\equiv SiX]{RC(O)X} \equiv SiOC(S)R \xrightarrow[-\equiv SiX]{RC(O)X} [RC(O)]_2S \quad (19)$$

R=Me, Ph; X=Cl, Br

Table 3. Reactions of hexamethylcyclotristilathiane with proton donors REH.

REH	Reagent ratio $(Me_2SiS)_3$: REH	Reaction conditions	Product (yield, %)	Refs.
H_2O	2:9	alkaline hydrolysis, Δ	$HOSiMe_2OSiMe_2OH$	[26]
BuOH	1:6	70–80°, 2 h	$Me_2Si(OBu)_2$ (78)	[139]
$PhCH_2OH$	1:6	ditto	$PhCH_2OSiMe_2SH$ (49.3); $Me_2Si(OCH_2Ph)_2$ (15.2)	[139]
$HO(CH_2)_2NH_2$	1:6	20°, 0.5 h	$Me_2Si(OCH_2CH_2NH_2)_2$ (91)	[139]
$[HO(CH_2)_2]_2NH$	1:3	ditto	$Me_2SiO(CH_2)_2NH(CH_2)_2$—O— (82.5)	[139]
$HO(CH_2)_4OH$	1:3	100–110°, 2 h	$Me_2SiO(CH_2)_4O$ (92.5)	[139]
$HOCH_2CH(R)OH$	1:3	ditto	$Me_2SiOCH_2CH(R)OSiMe_2OCH(R)CH_2$, —O— R=H (98), Me (81.9)	[139]
PhOH	1:6	130–140°	$Me_2Si(OPh)_2$ (89.2)	[148]
o-PhC_6H_4OH	1:6	ditto	$Me_2Si(OC_6H_4Ph\text{-}o)_2$ (93.2)	[148]
ditto	1:3	70°, 3 h, toluene	$Me_2Si(OC_6H_4Ph\text{-}o)SH$ (71.2)	[148]
p-$PhNHC_6H_4OH$	1:6	70–80°	$Me_2Si(OC_6H_4NHPh\text{-}p)_2$	[140]
RR'I=NOH	1:6	50–70° C	$Me_2Si(OC{=}CRR')_2$, R=Ph, R'=H (94); R=R'=Me (91)	[152]
MeCOOH	1:6	50–60°	$Me_2Si(OCOMe)_2$ (86.8)	[146]
»	1:3	50°, 3 h, CCl_4	$[Me_2Si(OCOMe)]_2S$ (71.2)	[146]
RCOOH	1:6	50–60°	$Me_2Si(OCOR)_2$, R=Ph (76.1), $CH_2{=}C$ (Me) (88.4)	[146]
o-HOC_6H_4COOH	1:3	175°	Me_2Si—O—C_6H_4—C(O) (73) —O—	[146]
HOCORZCOOH	1:3	130–140°	—(—$Me_2SiOCOZOCO$—)$_m$—, Z=$(CH_2)_2$, m=7(99.7); Z=$(C_2H_4)_2$, m=7(90.2); Z=C_6H_4, m=S (91.2)	[146]
H_3BO_3	1:1	Δ	$HO(Me_2SiS)_2(Me_2SiO$—B(O)—O—$)_n$—H	[146]
ditto	1:2	Δ	$HO(Me_2SiS)[(Me_2SiO$—B(O)—O—$)_2]_n$—H	[146]
»	1:3	Δ	$HO(Me_2SiO$—B(O)—O—$)_{3n}$—H	[146]
$PhNH_2$	1:6	125°	$Me_2Si(NHPh)_2$ (86.2)	[154]
α-$C_{10}H_7NH_2$	1:6	»	$Me_2Si(NHC_{10}H_7\text{-}\alpha)_2$ (81.2)	[154]
p-$H_2NPhC_6H_4NH_2$	2:3	60–75°	$Me_2SiNHC_6H_4C_6H_4NHSiMe_2$ (80.6) —$NHC_6H_4C_6H_4NH$—	[154]

A study of the reaction of hexamethyldisilathiane with dicarboxylic acid halides showed that with fumaryl chloride, the cyclic sulphide is formed, whereas with the chlorides of adipic and sebacic acids, polyacyl sulphides are formed:[171]

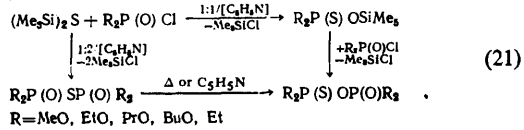


(20)

m = 4, 6

The reaction rate is increased in the presence of tertiary amines. Their catalytic action can be attributed to the formation of the N-acylammonium cation, which is more active in the exchange reaction than the original acyl halide.

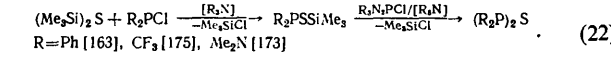
The chlorides of phosphorus(V) acids react similarly with organosilathianes:[61,173]



(21)

R=MeO, EtO, PrO, BuO, Et

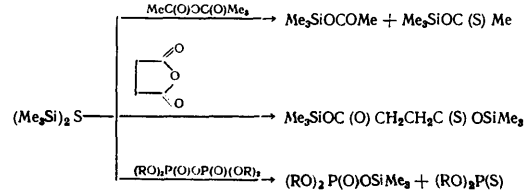
The halides of phosphorus(III) acids are more active than dialkyl phosphorochloridates towards hexamethyldisilathiane. The reaction involves the intermediate formation of silyl esters of phosphorus thio-acids:[174,175]



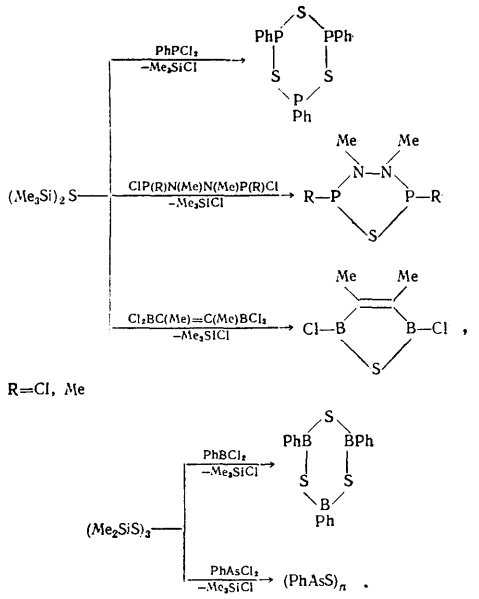
(22)

R=Ph [163], CF_3 [175], Me_2N [173]

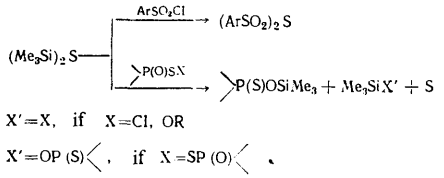
Dialkyl chlorophosphites [reaction (22)] give a mixture of products difficult to separate, formed by the thermal isomerisation of intermediate compounds and the final tetra-alkyl monothiopyrophosphites.[176,177] Carboxylic acid anhydrides and pyrophosphates undergo exchange reactions analogous to reactions (19)–(21):[61,171]



The reaction of the dichlorides of acids of phosphorus, boron, and arsenic with organosilathianes gives cyclic or polymeric products:[153,163,165]



Organosilathianes react equally readily with the halides of sulphonic acids,[61] phosphorylated sulphenyl chlorides, and their derivatives:[178]



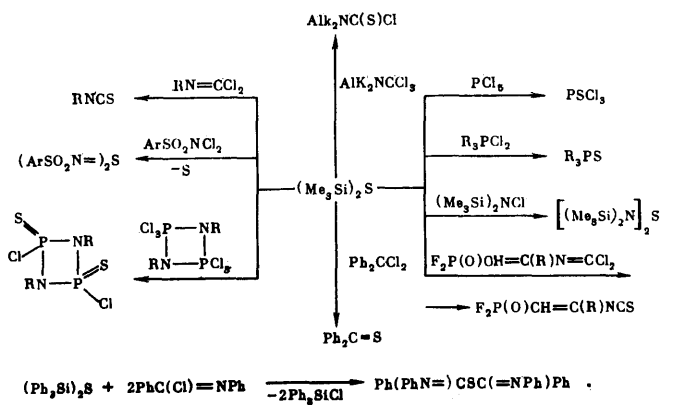
The exchange reaction of halogenogermanes with disilathiane and hexamethyldisilathiane gives mixed silyl germyl sulphides, which disproportionate when heated to give the symmetrical sulphides:[179]

$$(Me_3Si)_2S + H_3GeF \xrightarrow{-Me_3SiF} H_3GeSSiMe_3$$

$$(H_3Si)_2S + H_3GeCl \xrightarrow{-H_3SiCl} H_3GeSSiH_3$$

$$R_3SiSGeR'_3 \overset{\Delta}{\rightleftarrows} (R'_3Ge)_2S + (R_3Si)_2S \ .$$

Reactions of type (18) can be used to synthesise many sulphur compounds which are difficult to obtain:[61,103,164,180]



Thus exchange between organosilathianes and halogen-containing reagents with an E–X bond, where E is an element from groups I–VIII, and X = F, Cl, Br, I, makes reaction (18) a new general method for introducing sulphur into the molecules of inorganic, organic, and hetero-organic compounds.

Hexamethyldisilathiane reactions vigorously and exothermally with metal oxides[181] according to the scheme:

$$n\,(Me_3Si)_2S + MO_n \rightarrow n\,(Me_3Si)_2O + MS_n \qquad (23)$$
$$M=Ba,\ Pb,\ Mn,\ Zn,\ Ca$$

Cyclic silathianes are even more reactive in reactions of type (23). Thus hexamethylcyclotrisilathiane inflames spontaneously in its reaction with manganese dioxide even in a stream of nitrogen.[181]

In contrast to this, the passage of a mixture of oxides of nitrogen through a solution of hexa-alkyldisilathianes in ether does not lead to rupture of the Si–S–Si bonds, and the reaction products are bis-(trialkylsilyl) sulphones.[20]

Hexamethyldisilathiane undergoes an exchange reaction with phosphorus(V) oxide to give phosphorus(V) sulphide, tris(trimethylsilyl) phosphate, and tris(trimethylsilyl) thiophosphate:[61]

$$12(Me_3Si)_2S + 3P_4O_{10} \rightarrow 6(Me_3SiO)_3PO + 2(Me_3SiO)_3PS + P_4S_{10} \ .$$

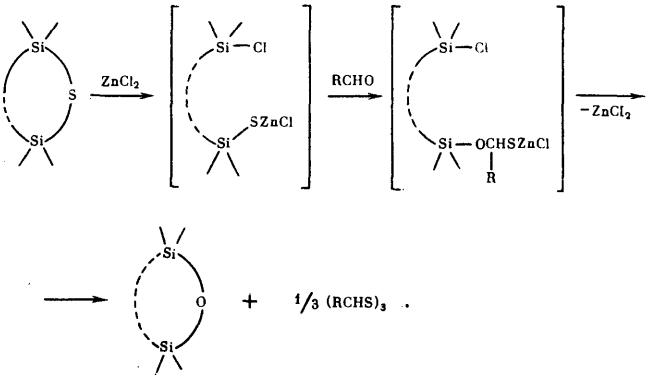
Phosphorus(V) sulphide in turn can also react with hexamethyldisilathiane to give the tris(trimethylsilyl) ester of trithiophosphoric acid.[84]

$$6(Me_3Si)_2S + P_4S_{10} \rightarrow 4(Me_3SiS)_3PS \ .$$

Organosilathianes react when heated with aldehydes and various perhalogenoketones;[183] the final products in the case of aldehydes are the products of the exchange reaction, siloxanes and thioaldehydes, and in the case of ketones the products of an insertion reaction. These data led to the proposal[182] of a general scheme for the reactions of organosilathianes with carbonyl compounds, including as an intermediate stage the formation of an unstable compound of type (IV), which subsequently decomposes to stable products by a four-centre mechanism. The introduction of halogen atoms, which have a strong electron-acceptor effect, into the molecule of the carbonyl compound stabilises the insertion product to such an extent that it can be isolated and characterised:[183]

$$(Me_3Si)_2S + RCHO \xrightarrow{50-80^\circ} \underset{(IV)}{[Me_3SiOCHRSSiMe_3]} \xrightarrow{-(Me_3Si)_2O}$$
$$\rightarrow [RCHS] \rightarrow {}^1/_3\,(RCHS)_3$$
$$R=Me,\ Et,\ Pr,\ Ph,\ p\text{-}O_2NC_6H_4,\ p\text{-}MeOC_6H_4 \qquad (24)$$
$$(Me_3Si)_2S + RR'CO \xrightarrow{70^\circ,\ 7\ d} (Me_3SiOCRR')_2S$$
$$R=CF_3,\ CF_2Cl;\ R'=CF_3.$$

In contrast to hexamethyldisilathiane, cyclic silathianes react with aldehydes at a higher temperature (140–150 °C) and in the presence of a catalyst ($ZnCl_2$) according to the scheme:[182]



The difference in the reactivities of the linear and cyclic organosilathianes towards aldehydes can be attributed to the difficulty of formation of an insertion product involving cyclosilathianes, a structure with many-membered rings is not characteristic for the insertion product.

Organosilathianes have been proposed as mild reducing agents for sulphoxides[61,184] and selenoxides.[61] The reaction apparently also takes place by the mechanism of reaction (24):

$$(Me_3Si)_2S + RR'E^+-O^- \xrightarrow[-(Me_3Si)_2O]{} RR'E + S$$
$$E = S,\ Se;\ R = Me,\ Et,\ Ph;\ R' = Me,\ Ph$$

In the reactions of hexamethyldisilathiane with various compounds of germanium, tin, and lead, exchange between the sulphur atom of the organosilathiane and an oxygen atom of the heteroorganic reagent is observed:[185]

$$(Me_3Si)_2S \xrightarrow[-Me_3SiOMe]{R_3MOMe} (R_3M)_2S$$
$$(Me_3Si)_2S \xrightarrow[-(Me_3Si)_2O]{(R_2M)_2O} (R_3M)_2S$$
$$(Me_3Si)_2S \xrightarrow[-(Me_3Si)_2O]{R_2MO} R_2MS$$

M = Ge, Sn, Pb; R = Et, Bu

Exchange between the sulphur atom of an organosilathiane and a hydrogen atom takes place as a result of reduction by metal hydrides.[23,30] Thus lithium hydride reacts with hexamethyldisilathiane in dioxan to give trimethylsilane.[23]

A study[30] of the stereochemistry of the reduction of 1,3-diphenyl-1,3-dimethyl-1,3-di-α-naphthyldisilathiane by lithium tetrahydroaluminate showed that at 20° the reduction takes place with inversion of the configuration, and at 85° racemisation takes place:

$$(+)\text{-}R_3Si^*SSi^*R_3 \xrightarrow{LiAlH_4} (+)\text{-}R_3Si^*H + [R_3Si^*S^-\ (LiAlH_3)^+] \xrightarrow{HCl}$$
(V)
$$\rightarrow [(+)\text{-}R_3Si^*SH] \xrightarrow{Et_2NH} (+)\text{-}R_3Si^*S^-\ H_2N^+Et_2$$
(VI)

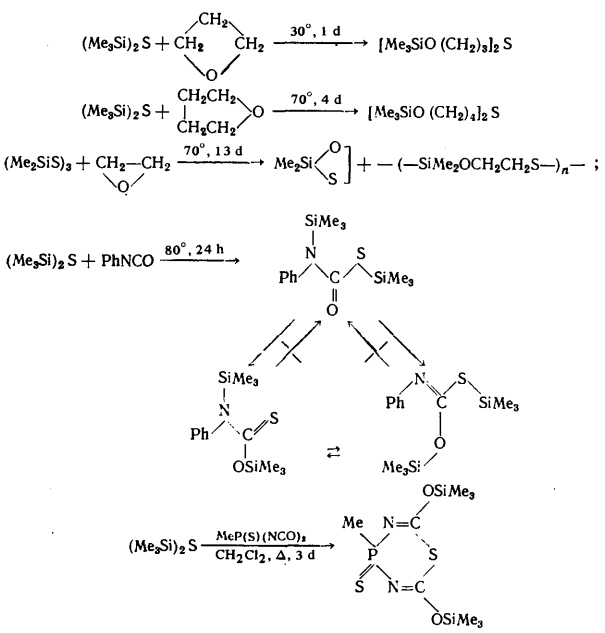
The structures of the complex (V) and the salt (VI) were proved by independent syntheses:

$$(+)\text{-}R_3Si^*SH + LiAlH_4 \xrightarrow[-78°]{-H_2} \ldots \xrightarrow[24\ h]{20\ °C} (V) \xrightarrow[Et_2O,\ -Bu_2O]{85°} (-)\text{-}R_3Si^*H$$
$$(+)\text{-}R_3Si^*SSi^*R_3 \xrightarrow{MeOH/Et_2NH} (VI)$$

2. Insertion Reactions

In hetero-organic chemistry, insertion reactions are usually classified according to the group being introduced, and are subdivided into 1,1-, 1,2-, ..., 1,*n*-additions to the substrate X–Y of the hetero-organic compound Z'_nM-Z, where Z'_n is the sum of the substituents, M a metal or non-metal, and Z the migrating group. In accordance with this generally accepted classification,[186] it is possible to systematise insertion reactions involving organosilathianes according to the type of addition (see start of section IV). In view of the limited number of known reactions of organosilathianes taking place by the insertion scheme (14), however, the reactions will be examined together, without breakdown into different types.

Oxygen-containing heterocyclic compounds,[187,188] organic[188] and organophosphorus[189] isocyanates, and arenesulphonyl isocyanates and arenesulphonyl isothiocyanates[190,191] split the Si–S bond in organosilathianes according to the schemes:



$$(Me_3Si)_2S + p\text{-}XC_6H_4SO_2N{=}C{=}Y \xrightarrow{80°,\ 24\ h} p\text{-}XC_6H_4SO_2N(SiMe_3)\text{–}C(SSiMe_3){=}Y \rightarrow$$
$$\rightarrow p\text{-}XC_6H_4SO_2N(SiMe_3)_2 + CSY$$
X=H, Me, Cl; Y=O, S

Thus exchange and insertion reactions involving organosilathianes are undoubtedly related, since, as can be clearly seen from the reactions of hexamethyldisilathianes with aldehydes, ketones, and arenesulphonyl isocyanates, the exchange reactions take place with the intermediate formation of the insertion product. Depending on the stability of this product, the reaction may either stop at the insertion stage or proceed further to give the exchange products.

An analogous mechanism can be proposed, for example, for the reactions of organosilathianes with oxides:

$$\equiv Si{-}S{-}Si\equiv + M{-}O \rightarrow [\equiv Si{-}O{-}M{-}S{-}Si\equiv] \rightarrow$$
$$\rightarrow \equiv Si{-}O{-}Si\equiv + M{-}S\ .$$

In conclusion, mention may be made of the only reaction involving organosilathianes that does not lead to splitting of the Si–S–bonds: the reaction of hydride-containing alkylcyclosilathianes with unsaturated compounds in the presence of $H_2PtCl_6.6H_2O$:[132,192]

$$[R(H)SiS]_3 + CH_2{=}CR'R'' \longrightarrow [RSi(CH_2CR'R'')S]_3 + [RSi(CR'R'')S]_3$$
(Me)

V. POSSIBILITIES FOR THE PRACTICAL APPLICATION OF ORGANOSILATHIANES

The first mention in the patent literature of the possible use of organosilathianes appeared in 1952, when they were patented as heat-stabilisers and anti-foaming agents for mineral oils[193] and lubricating materials.[194] In 1953, a patent was published on the use of organosilathianes as fungicides, insecticides, and additives to siloxanes.[26] It has been reported[195,196] that compounds containing an Si–S bond promote the droplet condensation of steam. Because of the difficulty of obtaining organosilathianes, however, the question of their practical utilisation remained open for a long time.

The main fields of application of organosilathianes were established only after convenient and effective methods had been developed for synthesising compounds with varied structures containing the Si–S–Si fragment[52,53,57,62,197] and their principal properties had been studied.[22,40,61,197,198]

Organosilathianes are the closest structural analogues of organosiloxanes, but unlike the latter, they are extremely active in reactions involving the heterolytic splitting of the Si–S–Si bonds. Thus the possible application of polymers containing only silathiane bonds is limited. Moreover, unlike siloxanes, organosilathianes do not form homopolymers with a high molecular weight.[63–65] Thus the main efforts of research workers have been directed towards the synthesis of new heteropolymers containing Si–S–Si bonds. A method for obtaining these heteropolymers is based on the reactions of cyclic silathianes and silathiaoxanes with boric, phosphoric, and phosphorous acids and their salts.[197–200]

The synthesised bora- and phosphasilathiaoxanes are liquid products, which have the advantage over their analogues the bora- and phosphasiloxanes that they can be uniformly distributed in rubber in sufficient quantities.[197–200]

The use of borasilathiaoxanes in heat-resistant self-cross-linking resins improves the technology of the resin mixtures and their autohesion properties, and leads to milder vulcanisation conditions (a decrease in the irradiation dose).[198–200]

Siloxane sealants modified by phosphasilathiaoxanes have improved thermal stability and improved adhesion and physicomechanical properties.[198–200] Moreover, organosilathianes can be used to modify the properties of not only organosilicon polymers, but also organic polymers. Thus a study [201] of the possible use of hexa-methylcyclotrisilathiane as a stabiliser in the thermal and radiation ageing of polymethyl methacrylate showed that the stabilising effect of this cyclotrisilathiane is particularly marked at high radiation doses and at the temperature of the start of the decomposition.

The high reactivity of organosilathianes towards proton donors is responsible for their application primarily as reagents for silylating inorganic, organic, and hetero-organic compounds.[30,61,71,79,80,132–165,202–205]

A study of the silylating power of organosilathianes indicated that their efficiency is greater than that of traditional silylating agents based on compounds with a $\equiv$Si–X bond, where X = H, Cl, NR_2.[61]

One of the main advantages of organosilathianes as silylating agents is the simplicity of the silylation process, which is carried out by mixing and heating the starting materials (30–120 °C) for a short time (0.5–3 h) to give a high yield (70–98%) of the silyl derivatives. The course of the reaction is conveniently followed gas-volumetrically from the quantity of hydrogen sulphide formed. The reaction does not require a large excess of the proton donor or the use of catalysts and solvents. Moreover, organosilathianes can be used for the effective selective silylation of proton donors containing two or more active groups in the molecule.

Organosilathianes may prove to be equally useful for introducing a sulphur atom into the molecules of organic and hetero-organic reagents,[57–62,103,153,170–175,180,204] and also as mild reducing agents for a number of oxygen-containing compounds.[61,184]

Thus the progress made in the application of organosilathianes in polymer chemistry and in preparative organic synthesis show the undoubted promising possibilities provided by further studies of the practical application of organosilathianes.

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While the present manuscript was being prepared for printing, the following papers were published, and reference to these provides a valuable supplement to the material examined above: the reduction of oxides of sulphur, selenium, and tellurium by hexamethyldisilathiane, obtained *in situ*;[203] the use of the boron trichloride–hexamethyldisilathiane system for the conversion of carbonyl compounds into thiocarbonyl compounds;[204] the synthesis of cyclosilaselenosilathianes by the insertion of sulphur and selenium into octamethyltetracyclosilane;[205] the synthesis of diacetoxydisilathiane by the photochemical thiolysis of methyl(vinyl)diacetoxysilanes—the first example of the conversion of a silicon–oxygen bond into a silicon–sulphur bond;[206] the reactions of hexamethyldisilathiane with compounds containing an element–chlorine bond;[207] the synthesis of functionally substituted organosilathianes;[208] organosilathianes in organic synthesis;[209] the reaction of hexamethyldisilathiane with phosphorus(V) oxide;[210] organosilathianes as silylating agents;[211] the mass spectrometry of organocyclosilathianes;[212] the synthesis of low-coordination compounds of silicon by the thermal decomposition of cyclosilathianes;[212–214] and the molecular and crystal structure of tetramethylcyclodisilathiane.[215]

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The Structure and Properties of Highly Conducting Polyacetylene Complexes

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The physicochemical characteristics of polyacetylene and its charge-transfer complexes have been examined. Data on the structural, electrical, magnetic, and optical properties have been discussed from a single viewpoint. Particular attention has been paid to a critical analysis of the soliton concept in relation to the structural and electrophysical properties. The probable mechanisms of the conductivity of polyacetylene have been examined.
The bibliography contains 118 references.

CONTENTS

I. Introduction 461
II. Electronic structure 462
III. Electrical properties 464
IV. Magnetic properties 466
V. Optical Properties 468
VI. Probable mechanisms of conductivity 469
VII. The structure of the conducting phase 471

I. INTRODUCTION

The first accurately solvable theoretical models used to study the electrical and magnetic properties of a solid were one-dimensional chains (for example the familiar models of Peierls, Ising, and Heisenberg). These one-dimensional models remained mathematical abstractions until the nineteen-seventies, when Shchegolev[1] drew attention to the possibility of obtaining real quasi-one-dimensional systems by chemical methods. This was soon followed by the description of the quasi-one-dimensional charge-transfer complex (CTC) TTF–TCNQ,† in which were detected not only metallic conductivity but also superconducting fluctuations close to 60 K. Although the latter were not confirmed, the sensational character of the report led to a rapid increase in the number of published papers on systems of small dimensions with unusual electrophysical properties.[2]

Polyconjugated organic polymers were the subject of detailed studies even in the nineteen-sixties, and important contributions to their study were made by Berlin, Cherkashin, Davydov, Liogon'kii, and others.[3,4] Almost all polyconjugated systems were found to be paramagnetics and semiconductors with interesting optical properties. Because of the low quality of the specimens, the impossibility of obtaining single crystals, and the uniformity of the principal characteristics, however, interest in the electrophysical properties of conjugated organic polymers decreased sharply in recent years. The renewal of interest in these materials is probably due to the discovery of the interesting properties of the inorganic polymer polythiazyl $(SN)_x$, whose single crystals show metallic conductivity under ordinary conditions, and become superconducting at T_c = 0.3 K.‡ Thus it has been shown that among polyconjugated compounds there are systems which do not contain a metal and which at the same time show metallic and even superconducting properties over a wide temperature range.

This striking result led to the discovery[5] of the unusual properties of the simplest polyconjugated organic polymer, polyacetylene $(CH)_n$, doped with electron donors or acceptors. As a result of doping, the specific conductance σ changes by many orders of magnitude, and, depending on the doping level, may take different values, typical of dielectrics, semiconductors, and even metals[6] (Fig.1).

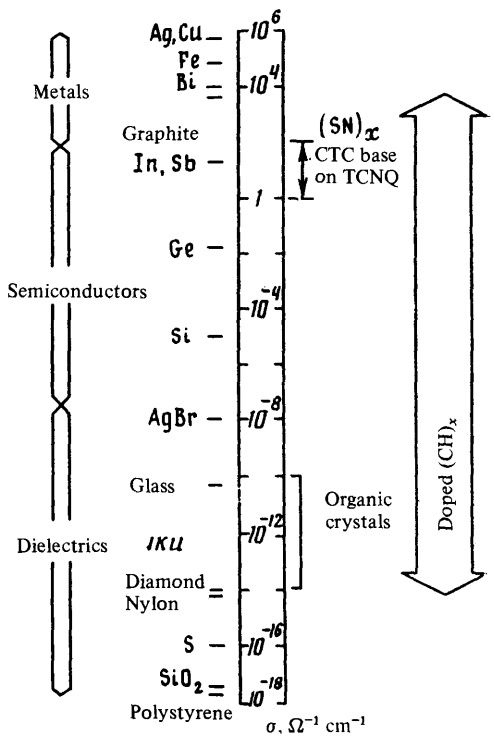


Figure 1. The specific conductance of doped PA and typical solids.[6]

† Here and subsequently, TTF = tetrathiafulvalene, and TCNQ = tetracyanoquinodimethane.

‡ See M.M.Labes, P.Love, and L.F.Nichols, Chem.Rev., 1979, 79, 1.

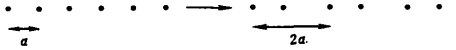
The simplicity of the molecular structure of polyacetylene (PA), the ease of obtaining high-quality films, and the possibility of varying their properties in planned fashion drew particular attention to PA. PA apparently provides an unprecedented example of a chemical compound whose properties have been studied using almost the entire range of physical methods. In theoretical chemistry and physics, PA provides a unique testing ground for that most modern (an popular) concept, the theory of solitons.

The main aim of the present review is to analyse the soliton concept, which is exotic in chemistry, but extremely popular in present-day physics. Since the soliton models of PA and analogous systems claim to provide a unique and systematic description and explanation of the principal physical properties, their examination is of considerable interest for the experimental and theoretial chemistry of conjugated polymers. The total number of published papers on PA is very large; it reached a maximum in 1983–1984, but had decreased considerably by 1987, while remaining high compared with other conducting polymers. Since PA is the prototype of all poly-conjugated organic systems, it is hoped that the present review will lead to a better understanding of other polymers such as poly-*p*-phenylene, polypyrrole, polythiophen, etc.

II. ELECTRONIC STRUCTURE

For many years the efforts of chemists have been concentrated on the synthesis of polyconjugated compounds with the longest possible chain. These studies have been based on both simple quantum-chemical calculations by the Hückel method and experimental data on the optical and electrical properties of model low-molecular-weight systems, according to which the width of the energy gap E_g (that is the energy of the transfer of a π-electron from the ground state to the lowest excited singlet state) and hence σ increase with increase in the number of conjugated units $N_{C=C}$. In the limiting case as $N_{C=C} \to \infty$, the electrons should be completely delocalised, the bonds beween the C atoms should be completely equivalent, and the ground state of the polymer should become metallic. Among the vast number of compounds synthesised, however, it has not been possible to discover one whose electrophysical properties are not semiconducting. This has led to a number of phenomenological explanations, details of which can be found in familiar monogaphs.[3,4] A significant feature is that all the explanations have taken into account not the intrinsic electronic properties of the polyene chain but numerous secondary factors, chiefly conjugation defects and disorder in the supermolecular structure.

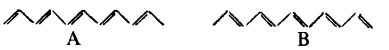
This situation apparently arose because of the sharp separation between the chemistry of macromolecular compounds and solid-state physics. At the same time, for physicists, this problem had been settled long before: the impossibility of the metallic state in one-dimensional systems follows from Peierls' theorem, according to which a regular one-dimensional chain of atoms is unstable with respect to deformation leading to doubling of the lattice period *a*:



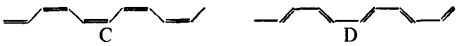
The change from a structure with equalised bonds to a structure with alternation of the bonds is called a Peierls transformation. In the band theory of solids, in the Peierls phase, the conductivity band is split exactly in the middle, as a result of which this phase is dielectric. The Peierls transformation is energetically favourable as a result of the lowering of the total energy of the lattice. This instability is characteristic of any one-dimensional metal, and the nature of the distortions is determined by the degree of filling of the conductivity band: if $1/n$ is the degree of filling of the band, then the change to the dielectric state is associated with *n*-merisation of the lattice. Since for PA, $n = 2$, there should be alternation of the double and single bonds in the chain. The alternation of the bonds in PA can now be regarded as a factor established experimentally from X-ray[7] and electron[8] diffraction data and from solid-state NMR spectra;[9,10] the difference between the lengths of the double and single bonds is 0.06–0.08 Å.

Thus an ideal crystal of PA should be a dielectric. At the same time, the experimental values of σ show a wide scatter, $10^{-5}-10^{-12}$ Ω^{-1} cm^{-1}.[11,12] The comparatively high values of σ are due to defects of different kinds in the molecular and crystal structure of real specimens; the paramagnetic defects are of particular interest. Polyacetylene exists as *cis*- and *trans*-isomers; the former is thermodynamically stable only at low temperatures, and is the main product of the catalytic polymerisation of acetylene by the most widely used method of Shirakawa.[13] The paramagnetism of PA is due entirely to the presence of the *trans*-isomer, and on thermal isomerisation (which is irreversible, because of side reactions leading to cross-linking of the chain and partial degradation of the polymer), the increase in the proportion of the *trans*-segments is accompanied by an increase in the concentration of spins and an increase in σ.[12]

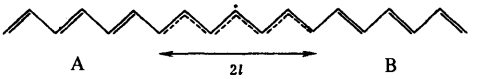
For the subsequent discussion it is important to note that the ground state of *trans*-PA is doubly degenerate: change in the alternation sequence does not alter the energy. Thus the existence of two resonance phases A and B of equal energy is possible:



There is no degeneracy in *cis*-PA: change in the alternation sequence converts the *cis*-transoid phase C into the less stable *trans*-cisoid phase D:



It was the energetic equivalence of the phases A and B that provided the basis of the solution model of *trans*-PA, better known as the Su–Schrieffer–Heeger (SSH) model.[14] Strictly speaking, a soliton is an isolated wave, which retains its structure after collision with any other isolated wave of the same type. In solid-state physics, the term solitons is usually employed to describe non-linear excitations leading from one potential energy minimum to another with the same energy, and they are regarded as quasi-particles. In the case of *trans*-PA, a soliton is a topological defect in the alternation, extending over several bonds, so that the phase A is gradually converted into the phase B:



In the SSH model, the *trans*-PA chain is represented by a one-dimensional lattice with an elastic constant *K*, at each site of which there is one π-electron and phonon interactions are taken into account by a Hamiltonian of the form:[14]

$$H = \sum_{n,S}^{N} \beta_{n,n+1} (a^{+}_{n,S} a_{n+1,S} + a^{+}_{n+1,S} a_{n,S}) + \frac{1}{2} K \sum_{n} (u_n - u_{n+1})^2$$

The first summation is the Hückel Hamiltonian for N electrons, written in the representations of secondary quantisation, where $\beta_{n,n+1}$ is the resonance integral of the bond between the atoms with numbers n and $n + 1$, and $a^{+}_{n,S}$ *and* $a_{n,S}$ the operators of the generation and annihilation of π-electrons in the states with number n and spin S. The second summation represents the energy of the elastic lattice with displacements u_n of the lattice sites from their equilibrium positions. Thus $\beta_{n,n+1} = \beta_0 - \alpha(u_{n+1} - u_n)$, where α is the electron–phonon interaction constant. If only the electronic energy is taken into account, the one-dimensional lattice will be unstable with respect to Peierls doubling of the lattice period, and will be

transformed into the state with alternation of the bonds. Doubling corresponds to the condition $u_n = (-1)^n u_0$, where u_0 is the displacement of the lattice sites in the defect-free chain of *trans*-PA. Thus a gap $E_g = 2\Delta = 8\alpha u_0$ is produced between the valence band and the conductivity band. The soliton excitations are introduced by means of the function

$$\Delta_n = \Delta \text{th}(na/l) \quad (1)$$

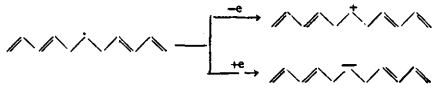
where l is the half-width of the soliton, whose wavefunction has the form

$$\Phi_n = l^{-1/2} \cos(\pi n/2) \text{ sech } (na/l) \quad (2)$$

Thus in the SSH model, solitons appear not from the internal structure of the solution, but as localised electronic states in the centre of the gap with the given topology of the defect. In view of the considerable computational difficulties, the SSH Hamiltonian allows only a numerical solution. When the parameters E_g + 1.4 eV, band width $4\beta_0$ = 10 eV, and K = 21 eV Å^{-2} are used, the SSH model gives the energy of the soliton $E_s = 2\Delta/\pi \simeq 0.42$ eV and $l = 2\beta_0 a/\Delta = 7a$. The relatively large size of the soliton compared with the lattice period shows that the discrete character of the lattice plays practically no part, and that the energy of the capture of a soliton by a lattice site does not exceed several meV. The effective mass of the soliton is only a few times greater than the mass of the electron, so that the soliton has a very high mobility.

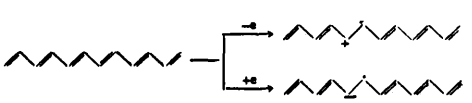
In the continuum model[15] [$na = x$; $\Delta_n \rightarrow \Delta(x)$], the function (1) strictly describes the configuration of the ground state with the boundary conditions $\Delta(x) \rightarrow \pm\Delta$ as $x \rightarrow \pm\infty$. Unlike the discrete SSH model, the continuum model makes it possible to obtain analytical solutions. In most cases the results of calculations using the two models agree qualitatively, although the concrete definition of the structure of the soliton in the discrete model makes it possible to take account of various fine effects.

The solitons just examined have spin, but not charge, so that they are responsible for the paramagnetism of PA, but are not current carriers. The role of carriers is played by spin-free charged solitons, which should be produced by the reaction of a donor or acceptor of electrons with defect chains of *trans*- PA:

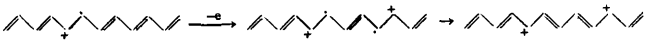


From a chemical viewpoint, neutral solitons S$^{\cdot}$ are radicals, positive solitons S$^+$ are carbocations, and negative solitons S$^-$ are carbanions, and in all cases the electron density is delocalised over a certain section of the chain with length $2l$. Fig.2 illustrates the situation in the representations of the band structure of solids.

Thus PA becomes a conductor as a result of doping and the associated rearrangement of the electronic structure, and not as a result of a phase transformation of the chain into a metastable state, which is not produced in compounds of this class. In other words, the electron or hole formed as a result of doping and charge transfer, after a certain characteristic time, are converted into a localised state with the formation of a soliton. If the doping reaction involves not only defect chains having spin but also defect-free chains, then solitons should be generated in pairs.[14] Numerical calculation[16] shows that with slight doping, the energetically preferred formation is not a non-bonded soliton–soliton pair S$^{\pm}$–S$^{\cdot}$ but a polaron P$^{+\cdot}$ (in other words a radical-ion), representing a bound state:



The phases of the alternation on the two sides of the soliton are opposed, whereas the formation of a polaron does not lead to changes in the phases. Two symmetry levels now appear in the energy gap (Fig.2), one of which is situated ~0.3 eV above the top of the valence band, while the other is situated at the same distance below the bottom of the conductivity band. On further doping, two processes compete with one another; the polaron states begin to form a band, and neighbouring polarons may recombine to give spin-free bipolarons (carbodications):



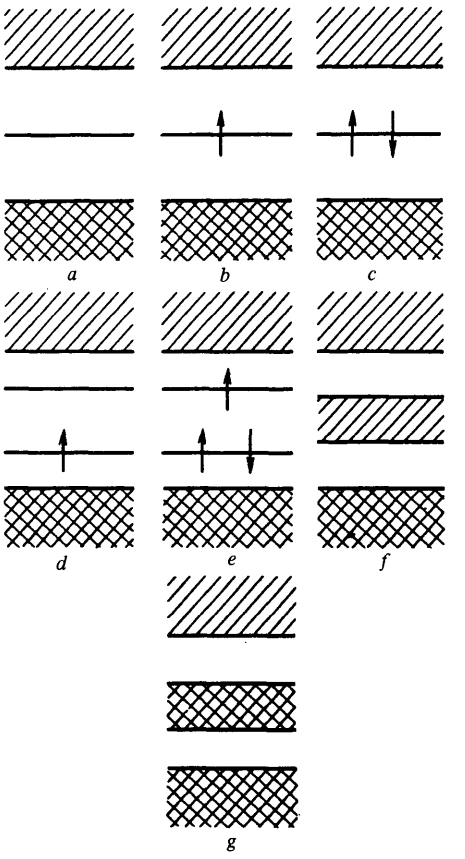


Figure 2. The band structure of states of the soliton type with charge q and spin S: *a*) positive soliton S$^+$ ($q = +e$, $S = 0$); *b*) neutral soliton S$^{\cdot}$ ($q = 0$, $S = 1/2$; *c*) negative soliton S$^-$ ($q = -e$ $S = 0$); *d*) positive polaron P$^+$ ($q = +e$, $S = 1/2$); *e*) negative polaron P$^-$ ($q = -e$, $S = 1/2$); *f*) soliton lattice S$^+$ ($q = Nye$, $S = 0$); *g*) soliton lattice S$^-$ ($q + -Nye$, $S = 0$).

Because of the degeneracy of the ground state of *trans*-PA, the bipolarons are unstable, and dissociate to give charged solitons forming a conductivity band within the gap (Fig.2). The conductivity is now due not to jumps between localised soliton states but to the soliton band. This band subsequently becomes broader, and finally joins up with the top of the conductivity band and the bottom of the valence band, the gap collapses, and the highly doped PA becomes a quasi-metal with ordinary electronic conductivity.

Thus for highly conducting complexes of PA, two fundamentally different conductivity mechanisms are postulated. The first is due to the movement of quasi-particles—spin-free charged solitons (or bipolarons)—which are combined with distortions of the lattice and which form a band (either completely filled or unpopulated) within the gap. The novel and unique character is revealed in highly doped specimens and is associated with the ordinary movement of electrons as a result of the overlap of the conductivity, valence, and soliton bands.

The polaron model is more general than the soliton model, since it does not require degeneracy of the ground state. This requirement, generally speaking, is extremely strict, and is not satisfied even for *cis*-PA. Nevertheless, the electrophysical properties of the two isomers are completely analogous; moreover, analogous properties are shown by poly-*p*-phenylene, polypyrrole, and other polymers, for which there is no degeneracy. Between the soliton and polaron models of PA, however, there is a deep internal relationship, which follows from relativistic φ^4 field theory;[17] a universal method for obtaining soliton, polaron, and other quasi-particle solutions has been proposed, for example, in Ref.18. The large number of modifications of the SSH model will not be discussed (the interested reader can find details in a published review[19] and the references therein), and attention will be concentrated on the cardinal question of whether the soliton theory is in fact necessary and sufficient to explain the properties of PA and, in the wider sense, all conducting polymers.

III. ELECTRICAL PROPERTIES

The general character of the changes in the static electrical conductivity σ when PA is doped with various typical acceptors to the maximum levels attainable experimentally is shown in Fig.3,[20] where y denotes the number of moles of dopant per mole of CH units. Thorough studies[21] showed that the detailed form of the $\sigma(y)$ relationship is determined by the previous history of the specimens: the method used to synthesise the PA, the isomeric composition, the type of dopant, and, to the greatest extent, by the method of doping. In general, it is assumed[21] that the slower the introduction of the dopant, the narrower the range of values of y within which the main increase in the electrical conductivity takes place. For example, when *trans*-PA is doped with iodine vapour at $p \leqslant 0.1$ mmHg, σ increases by a factor of 10^4 in the range $10^{-3} \leqslant y \leqslant 10^{-2}$.[21] On the other hand, the $\lg\sigma - \lg y$ graphs obtained by doping *cis*- and *trans*-PA with AsF_5 vapour at different pressures[21] were practically linear throughout the range of values of y, and the same results were obtained when PA was doped rapidly (p = 0.3 mmHg) with iodine vapour.[22] The dependence of the thermo-EMF on the doping level is also determined by the rate of doping;[21,23] the lower the rate of doping of PA, the narrower the range of values of y within which the thermo-EMF decreases from the values typical of semiconductors ($\sim 10^3$ μV K^{-1}) to the values typical of metals (~ 10 μV K^{-1}).

The observed effects are usually attributed to the more or less uniform distribution of the dopant throughout the volume of the PA specimens. It is assumed that the most uniform distribution is achieved with so-called cyclic doping. In this method, the exposure of the film of PA to the vapour of the dopant, for example AsF_5 (at T = 143 K, $p < 0.1$ mmHg), is alternated either with evacuation or with freezing-out the non-absorbed AsF_5 at 7 K,[21,23,24] and this procedure is repeated until the required doping level is achieved. Thus the experimental justification for the theory of uniform doping is the exceptional sensitivity of various electrophysical characteristics to the doping method: the more uniform the distribution of the dopant, the sharper the semiconductor–metal transition.

At the same time, it follows from even simple estimates of the entropy effects and the energy of lattice deformation on doping[25] that aggregation of the dopant in stacks or layers is energetically preferable to its random distribution (with the possible exception of the small Li^+ ions). Direct measurements of the distribution profiles by electron-probe X-ray microanalysis[26] in all cases showed an extremely non-uniform distribution of the dopants at low values of y even in thin PA films (~ 10 μm), and relatively uniform distribution was achieved only by doping to y_{max}. The effect achieved by cyclic doping is not clear; it is not fully understood how repeating the low-temperature cycles is able to achieve the required uniformity.

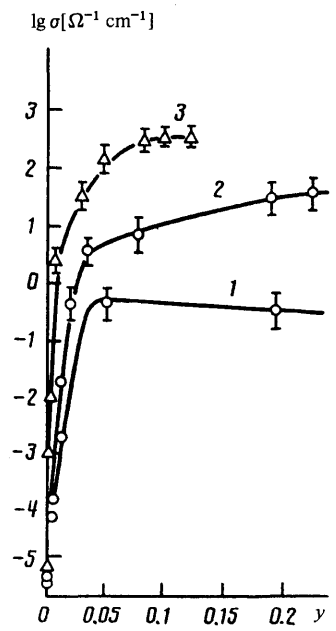


Figure 3. Dependence of the electrical conductivity of PA on the doping level;[20] *1*) $(CHBr_y)_x$, *2*) $(CHI_y)_x$, *3*) $[CH(AsF_5)_y]_x$.

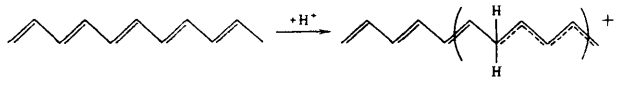
Thus diffusion is an activated process, and its rate decreases exponentially with temperature. It is significant that the characteristic distribution profiles of the dopant into the bulk of the specimens remain completely unchanged even when the films are kept for one week in a dynamic vacuum.[27] This phenomenon is probably due to fixation of the dopant as a result of chemical reactions, so that free diffusion stops. For the same reason, deviation from Fick's law is observed, as shown in experiments[28] on the kinetics of diffusion.

Unfortunately, there are extremely few published data on the chemistry of the reactions of PA with dopants. Extensive photoelectron, Mössbauer, and Raman spectroscopic data make it possible to formulate the most extensively studied reactions as follows:

$$2(CH)_x + 3y\,AsF_5 \rightarrow 2[(CH)_x^{y+}(AsF_6^-)_y] + y\,AsF_3$$
$$(CH)_x + 2y\,FeCl_3 \rightarrow [(CH)_x^{y+}(FeCl_4^-)_y] + y\,FeCl_2$$
$$2(CH)_x + 3y\,I_2 \rightarrow 2[(CH)_x^{y+}(I_3^-)_y]$$

The actual situation, however, is much more complex than indicated by these simple equations. After doping with AsF_5, the composition of the specimens usually corresponds to the formula

$[CH(AsF_n)_y]_x$, where $5 \leqslant n \leqslant 6$,[29] depending on the doping conditions. In addition to I_2 molecules, $(CHI_y)_x$ contains the ions I_5^-, I_3^-, and I^-,[30] and when bromine is used as dopant, most of it adds on across the double bonds of PA, forming saturated segments $-CHBr-CHBr-$.[31] Some dopants undoubtedly form covalent bonds with PA, as shown for bis(fluorosulphuryl)peroxyl [32] and trimethyloxonium salts, which are effective CH_3^+ cation donors.[33] Doping by protic acids which are not oxidising agents, for example, HF, apparently takes place by the same mechanism:[34]



In published discussions of the $\sigma(y)$ relationships, however, the independent variable y taken is always the total analytical concentration of the dopant, which is found either gravimetrically or (for the smallest values of y) using tracer atoms. It is assumed *a priori* that all the absorbed dopant forms a highly conducting complex with PA. This assumption is in general incorrect; spectrophotometric analysis of the equilibria by the Benesi–Hildebrand method in PA–I_2 [35] and PA–Br_2 [36] systems showed that the composition of the conducting complexes corresponds to the formula $[(CN)_n(X_2)]$, where X = I or Br, and $(CH)_n$ is a segment of the continuous conjugation ($n < x$). Thus S_3^- ions may also be produced by side reactions which are not related to the formation of conducting complexes. Additional evidence in support of this conclusion is apparently provided by data on the thermal desorption of iodine from $(CHI_7)_x$:[37] treatment of the specimens at 383 K for 105 min lowered the conductivity by a factor of 10^4 with a decrease in y by a factor of 5, but at the same time the intensity of the band at 107 cm^{-1} in the Raman spectrum due to I_3^- ions increased by a factor of 14.

The formation constants of $[(CH)_n(I_2)]$ and $[(CH)_n(Br_2)]$ are 64 $mole^{-1}$ and 8 $mole^{-1}$ respectively, and the concentrations of the active states in PA accessible for complex formation at 0.4 mole dm^{-3} for I_2 and 0.9 mole dm^{-3} for Br_2.[35,36] Thus many of the properties of doped PA are determined by the chemical character of the dopant. Thus it has been shown[35] that for the overall formula $(CHI_{0.25})_x$, the equilibrium composition which is entirely responsible for the electrical conductivity corresponds to the formula $(CHI_{0.008})_x$.

Thus for the vast majority of dopants, the true concentration dependence $\sigma(y)$ must be regarded as unknown. The same is true of the concentration dependence of the thermo-EMF. For its determination, it is necessary to take as independent variables not the total but the equilibrium concentrations of the dopants. Thus use of the equilibrium concentrations may lead to radical changes in the established relationships between the composition and properties of PA. From the classical relationship for semiconductors

$$\sigma = c\mu e \qquad (3)$$

where c is the concentration of the carriers, μ their mobility, and e the charge of the electron, it follows that σ is linearly dependent on the equilibrium concentration of the conducting complex. In fact, the dependence is exponential,[35,36] as is characteristic of the Mott mechanism of conductivity in disordered solids, which involves jumps of variable length between localised states.[38] Data obtained at room temperature[35,36] show very good agreement (correlation coefficient 0.995) with the Mott law $\sigma \sim \exp(-T^{-1/4})$ throughout the range studied, $0.007 \leqslant y \leqslant 0.25$. Thus the use of the equilibrium concentrations shows that there are no signs of a semiconductor– metal transformation and hence of a change in the mechanism of the conductivity, at least in this range of nominal values of y.

Representation of the data[35,36] in the form of the usual $\sigma(y)$ relationships gives typical *S*-shaped curves. On these graphs it is possible to distinguish three regions. In the first ($y \lesssim 10^{-4}-10^{-3}$), the $\sigma(y)$ dependence is weak; in the second ($10^{-3} \lesssim y \lesssim 10^{-2}$), the $\sigma(y)$ dependence is very strong, and this is interpreted as a semiconductor–metal transformation;[21,39] in the third, quasi-metallic, region, the conductivity is saturated (the values of y_{max} depend on the nature of the dopant). According to the soliton model, the change from one region to another should be accompanied by a change in the conductivity mechanism. The chief test for identifying the mechanisms is the temperature dependence of σ. Considerable efforts have been made to establish the $\sigma(T)$ relationships as accurately as possible, but in spite of the large amount of experimental data, no clear and systematic picture has yet been revealed. Typical graphs[39,40] are shown in Fig.4, and lead to two conclusions. Firstly, in all cases the temperature dependence is activational, but with increase in y the $\sigma(T)$ dependence becomes weaker (for dopants such as AsF_5,[39] $FeCl_3$,[41] and $(FSO_2O)_2$ [32] in the range 300–250 K, even a slight increase in σ, corresponding to the behaviour of metals, is observed). Secondly, there is no clearly defined phase transformation, which would have been revealed by an abrupt change in the $\sigma(T)$ relationship at a certain critical concentration of the dopant.

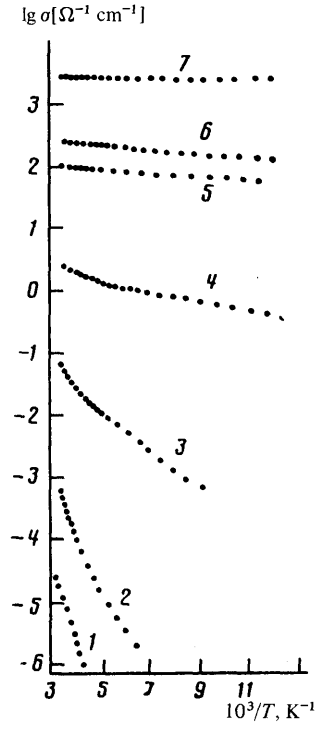


Figure 4. Temperature dependence of the electrical conductivity of $[CH(AsF_5)_y]_x$ [39] for y = 0 (*1*), 0.0028 (*2*), 0.0059 (*3*), 0.010 (*4*), 0.050 (*5*), 0.10 (*6*), and 0.14 (*7*).

For the analytical description of the $\sigma(T)$ dependence, different authors have used relationships of the form $\exp(-T^{-1})$, $\exp(-T^{-1/4})$, $\exp(-T^{-1/2})$, or T^x, where $x > 10$ (see the literature cited in Ref.11). This variety suggests that in fact, none of the proposed relationships is satisfied over a sufficiently wide range of temperatures. The same conclusion was reached after detailed $\sigma(T)$ measurements for $(CHI_y)_x$ specimens with different previous histories;[11] any functional relationship provided a satisfactory description of the experimental

data only in a more or less limited temperature range. It should be emphasised that, unlike the $\sigma(y)$ relationships, the $\sigma(T)$ relationships were found to be independent of the method used to dope PA.[42] If however the published conclusions[21,23] regarding the fundamental influence of non-uniform distribution of the dopant on the electrical properties of PA are accepted, then it is impossible to explain why these non-uniformities (or their absence) have no influence on the nature of the fundamentally more important $\sigma(T)$ relationships.

Generally speaking, the lack of agreement and often the direct contradiction between different experimental data on the electrical properties of PA are to a large extent due to the extremely complex morphology of the specimens, which makes correct measurements extremely difficult. In most photomicrographs obtained using the scanning electron microscope, PA films and powders appear as accumulations of disordered intertwined fibrils with a thickness of 10–80 nm and a length of tens of nm.[13,20] In films obtained by the standard method of Shirakawa, the volume fraction of the fibrils is ~40%. These fibrils in turn are made up of disordered, twisted, and intertwined micro-fibrils with a thickness of 3–5 nm.[43] On the other hand, transmission photographs show the presence of lamellae with a diameter of several tens of nm and a thickness of several nm; these lamellae combine in irregular stacks to form pseudo-fibrils.[6] High-resolution electron microscope data[44] show, however, that the morphological sub-units of both the original and the doped PA are globules with a diameter of 20–50 nm. These globules combine to form clusters, monolayers, or fibril-like formations, that is secondary structural elements. These elements then form tertiary structures: lamellae (monolayers lying on top of one another), loose networks, and their combinations with relative contributions determined entirely by the synthesis conditions. In freshly prepared PA, the globules are apparently joined to one another only by cohesive forces. Thus the polymerisation of acetylene in the presence of surface-active substances gives emulsions with spherical PA particles;[45] ultrasonic dispersal of the PA suspensions gives colloidal solutions.[46]

In one way or another, the basic structure of PA may become similar to a highly porous sponge with a specific surface of 35–60 $m^2\ g^{-1}$.[20,47] The electrical resistance of these specimens is made up of many terms which depend on temperature in different ways: the resistance of the inter-crystallite contacts within each fibril or globule, the resistance of the inter-fibril or inter-globule contacts, the resistance of the amorphous phase, and also terms determined by the high anisotropy of the three principal components of the specific conductance tensor. The macroscopic conductivity should naturally be determined by the largest of these resistance terms, but the real picture is complicated considerably when account is taken of geometric factors (the maximum specific resistance does not always correspond to the maximum resistance) and the fact that the ratio of the different components of the resistance may change with change in temperature. As a result, the $\sigma(T)$ relationship for non-crystalline specimens generally does not reflect the properties of the conducting complexes, and the data leave wide scope for speculation.

At the same time, unambiguous information on the intrinsic $\sigma(T)$ relationship can be obtained by the simple and elegant method of short-circuited potential electrodes (SPE), which eliminates the influence of the resistance of the inter-crystallite contacts and the small components of the specific conductance tensor.[48] The SPE method is qualitative, but it makes it possible to deduce the true temperature dependence of the largest of the components of the specific conductance tensor, by predicting the general course of the relationship for single crystals. The data obtained[49] by the SPE method at $T \geqslant 77$ K for highly conducting PA specimens (Fig.5) show that the true $\sigma(T)$ relationship has the form typical of metals, and is independent of the morphology of the PA. For $[CH(FeCl_3)_{0.06}]_x$, the SPE method established metallic behaviour as far as $T = 1.9$ K.[50]

IV. MAGNETIC PROPERTIES

The magnetic properties of PA have attracted particular attention from the very beginning. The experiments have been designed to answer the questions, of fundamental importance for the soliton concept, of whether the unpaired electrons are in fact highly mobile, whether their diffusion is chiefly one-dimensional, and whether at medium doping levels the paramagnetism disappears and the charge is carried by spin-free solitons.

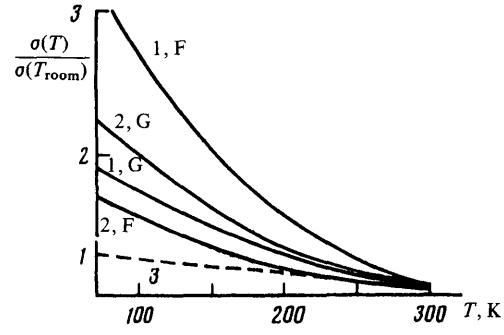


Figure 5. Temperature dependence of the reduced electrical conductivity, obtained by the SPE method;[49] *1*) $[CH(ClSO_3H)_y]_x$, *2*) $[CH(NOClO_4)_y]_x$ (*G* = globular PA, F = fibrillar PA); *3*) current-carrying silver paste.

An important factor for a theoretical description is how the spin density is distributed along the PA chain. The first source from which attempts were made to extract this information was EPR data.[51,52] The spectrum of PA contains an intense singlet with a width of several G, whose characteristics depend markedly on the previous history of the specimen.[12] The paramagnetic of PA is not associated with the charge carriers; treatment with ammonia lowers the conductivity by several orders of magnitude, but does not alter the EPR spectrum.[52] The experimental form of the EPR line is effectively reproduced[51] if the SSH spin wavefunction in form (2) is adopted. These and other similar calculations (see for example Refs. 53 and 54), however, do not take account of all the parameters determining the EPR spectra of π-electron radicals: the anisotropy of the *g*-value and the hyperfine interactions (HFI), the relative orientation of the tensor elements, and relaxation processes. Definite conclusions about the HFI and the number of nuclei involved in the interaction with the soliton can hardly be reached by modelling a singlet EPR line with an unresolved hyperfine structure (HFS). It has been correctly pointed out[55] that from the mathematical viewpoint, this is equivalent to solving one equation with many unknowns. As a result, a large number of wavefunctions, completely dissimilar to the function (2), are capable of reproducing the experimental EPR spectra equally successfully.

More reliable information on the distribution of spin density can be obtained by double electron–nuclear and triple electron–electron–nuclear resonance (ENDOR and EENTOR respectively): the ENDOR spectra are characterised by two and only two individual sets of HFI tensors for the C and H nuclei, and in the EENTOR spectra the relative intensities of the signals reflect directly the proportions of the nuclei involved in a given HFI.[56] It follows from ENDOR that in *trans*-PA, neighbouring C atoms are magnetically non-equivalent, and the spin densities on them are $\rho_1 = |0.06|$ and

$\rho_2 = |0.02|$, and from EENTOR it follows that they have opposite signs: $\rho_1 = +0.06$, $\rho_2 = -0.02$. Thus the unpaired electron must be delocalised over approximately 50 C atoms. This estimate seems too high. The accuracy of the determination of the absolute values of ρ, which depends on the choice of model used to calculate the components of the tensors, should not be overestimated; other data[57] indicate the value $\rho \geqslant 0.01$. The ratio $\rho_2/\rho_1 = -0.33$, found directly from the ENDOR line, is more correct.[58] Since negative values of ρ can appear only as a result of Coulombic interactions (the potential of the single-site electron–electron repulsion, estimated by the Hartree–Fock method, is ~ 3 eV [58]), it is clearly necessary to take account of electron correlations. The neglect of these correlations is probably the most significant unsatisfactory feature of the SSH model.

The main evidence of the unique character of the spins in *trans*-PA is the difference in the behaviour of the PA isomers, established in experiments[53] on the dynamic polarisation of the nuclei (DPN). These experiments involve the measurement of the dependence of the amplitude of the ^{1}H NMR signal at the nuclear Larmor frequency ω_n on the frequency of the microwave pumping, close to the electronic Larmor frequency ω_e. For mobile spins, the signal is amplified on pumping at a frequency ω_e (the so-called Overhauser effect). If however the spins are fixed (the frequency of their jumps is lower than ω_n), then the signal is amplified on pumping at a frequency $\omega_e + \omega_n$ and is weakened in the case of the frequency $\omega_e - \omega_n$ (the so-called solid-state effect). In fact, at room temperature, the Overhauser effect was observed in *trans*-PA, and the solid-state effect in *cis*-PA. Quantitative estimates of the dynamics of the spins and the dimensions of their diffusion[53] were obtained from the frequency dependence of the proton spin–lattice relaxation time T_{1H}. If the diffusion is one-dimensional, and the protons relax on the diffusing spins, then the relationship $f(\omega) = (2D_{||}\omega)^{-1/2}$ is fulfilled, where $f(\omega)$ is function of the spectral density, and $D_{||}$ the diffusion coefficient of the spins, related to the coefficient of translational diffusion by the relationship $D'_{||} = a^2 D_{||}$. From the experiments[53] it follows that $D_{||} = (3-6) \times 10^{13}$ s^{-1}, and the anisotropy of the spin diffusion is $D_{||}/D_{\perp} \simeq 10^6$.

The $T_{1H}^{-1} \sim \omega^{-1/2}$ relationship is not specific for one-dimensional diffusion, however, and may also be determined by nuclear spin diffusion (NSD) to fixed electronic spins, taking place by a reorientation of the nuclear spins with their subsequent relaxation on paramagnetic centres. Measurements of T_{1e} by the spin-echo method[59] show that the NSD model describes the experimental data no less satisfactorily than the one-dimensional model,[53] although the anisotropy and delocalisation of the solitons are completely neglected. The adequacy of the NSD model is confirmed by a large amount of ^{1}H, ^{2}H, and ^{12}C NMR data (see for examples Refs.60–62), and from spin-echo measurements[63,64] it follows that there are several types of paramagnetic defect. The high-resolution DPN spectra[10] reveal a solid-state defect in *trans*-PA even at room temperature. The great majority of continuous conjugation segments in *trans*-PA obviously do not contain highly mobile spins; otherwise, the movement of the solitons along the chains would have led to dynamic averaging of the bond lengths, that is to the suppression of alternation, and this does not agree with experiment. Although the discussion of the paramagnetic defects in PA is not complete, it may be concluded that the various magnetic resonance methods up to the present have provided information on those properties of the topological defects which are determined by their local structure, and not on their kinematic properties.

In non-doped PA, the paramagnetism obeys the Curie law. It would seem that proof of the inverse relationship between the charge and spin of the current carriers, predicted by the soliton model, should be easily obtained by measuring the dependence of the magnetic susceptibility on the doping level. Up to the present, however, irrefutable data have not been obtained. Measurements made by the Faraday method[65] and the Schumacher–Slichter method, based on a combination of NMR and EPR,[24] show a regular decrease in the temperature-independent Curie susceptibility χ_C and the absence of temperature-independent Pauli susceptibility χ_P when *trans*-PA is doped with moderate amounts of AsF_5. On the other hand, according to EPR data,[66] doping *cis*-PA leads to the rapid appearance of χ_P and its regular increase in proportion to y. A comparative EPR study[67] of the doping of *cis*- and *trans*-PA with AsF_5 only partly resolved the contradictions, by confirming that doping *cis*-PA is accompanied by an increase in χ_P, whereas in cyclically doped *trans*-PA, χ_P is negligibly small. These phenomena were again attributed to the non-uniform doping of *cis*-PA.

The quantitative determination of the concentration of spins [S$^\cdot$] in highly conducting materials encounters fundamental difficulties; increase in σ is accompanied by a greater skin-effect, produced when the thickness of the skin-layer and the characteristic dimensions of the specimen are comparable. The EPR line becomes asymmetrical, and no longer gives quantitative information on [S$^\cdot$]. Faraday's method,[65] which does not have this disadvantage, measures the total static magnetic susceptibility $\chi = \chi_D + \chi_C + \chi_P$, where χ_D is the diamagnetic component, which must be calculated from the Pascal constants. The accuracy of these calculations is undoubtedly low, because of the lack of accurate information on the state of the dopant in PA and the uncontrolled defects in the molecular structure of PA. Moreover, it is necessary to calculate the difference $\chi - \chi_D$; these quantities are of the same order of magnitude, and are greater than χ_C and χ_P by 1–2 orders of magnitude, so that the subtraction unavoidably leads to a high loss of accuracy.

The adequacy of the Schumacher–Slichter method[24] has not been established. For example, measurements of χ for $(CHBr_y)_x$ specimens by the Faraday method give $\chi_P \simeq 0$ for $0 < y < 0.02$, and $\chi_P \geqslant 4 \times 10^{-6}$ CGS units per mole of C for $y > 0.02$, whereas according to the Schumacher–Slichter method, $\chi_P \lesssim 10^{-8}$ CGS units per mole of C, irrespective of y.[68] The most convincing data are apparently EPR data[69] obtained for $[CH(AsF_5)_y]_x$ specimens prepared as extremely thin needles, which prevented complications resulting from the skin-effect. Irrespective of the isomeric composition of PA, at $T \lesssim 50$ K, superposition of two EPR lines with the same g-value, one narrow and one broad, was observed. The characteristics of the narrow line make it possible to assign it to conductivity electrons, responsible for χ_P. A remarkable feature is that χ_P increases regularly with increase in y in the same sense as the elecrical conductivity, from which it clearly follows that the current carriers in $[CH(AsF_5)_y]_x$ are classical in character. At the same time, the broad line is associated with localised electrons, responsible for χ_C; after the specimens have been treated with ammonia, only the broad line remains in the spectra. The same behaviour is characteristic of $[CH(SbF_5)_y]_x$.[69]

When PA is doped with iodine, the picture changes. EPR data[21,7] show a gradual decrease in the intensity of the signal and its complete disappearance in highly doped specimens, but the Faraday method[71] detects quite significant Pauli paramagnetism ($\chi_P \leqslant 2 \times 10^-$ CGS units per mole C). Other Faraday measurements,[72] however, do not show any significant χ_P, and the same result was obtained b EPR.[73] In Ref.73, however, in contrast to Refs.21 and 70, it was noted that with increase in the doping level, after the initial sharp decrease, the value of χ_C at $y \geqslant 0.1$ becomes constant. A more systematic picture was obtained when the EPR measurements were extended into the range of helium temperatures.[74] It was found tha not only the spin susceptibility, but also [S$^\cdot$], depend on temperatur and at $T \leqslant 10$ K, the values of [S$^\cdot$] are almost the same for the doped and non-doped specimens. Thus the absence of the EPR signal at high temperatures is directly related to the high conductivity; at y_{max}, the signal is not detected even at $T = 4.2$ K.

The characteristic features of the EPR in $(CHI_y)_x$, and also in $(CHBr_y)_x$, can be explained using the ideas developed for disordered semiconductors,[38,75] in which the EPR signal is usually due to defects in the crystal structure. This signal often disappears when the semiconductor is doped. On the other hand, an EPR signal due to lattice defects is not observed in any metal. This may be due either to the shielding by the conductivity electrons of the Coulombic repulsion between defect states having spins or to the hybridisation of the wavefunctions of localised electrons and conductivity electrons. Similarly, the magnetic properties of $(CHI_y)_x$ may be due to the interactions of localised and band states. Doping generates Pauli spins, which do not give an EPR signal, because of strong spin–orbit scattering on iodine, but which interact with Curie spins. As a result, the paramagnetism is determined both by Coulombic interactions between the localised states and by hybridisation of localised and band states; the increase in the hybridisation with increase in y may lead to the apparent disappearance of the local magnetic moment. In highly doped $(CHI_y)_x$, even at helium temperatures the conductivity is high, and no EPR signal is observed. This mechanism should be ineffective in $[CH(AsF_5)_y]_x$, because of the much weaker spin–orbit interactions at the As atoms, which are highly shielded by the F atoms coordinated to them. Thus published data[74] demonstrate directly the importance of the effects of localisation in in $(CHI_y)_x$ and $(CHBr_y)_x$.

There are much fewer experimental data on the magnetic properties of PA doped with donors. The most important results are those obtained[76] by EPR *in situ* in the liquid-phase doping of thin films of *trans*-PA using a solution of sodium-benzophenone in THF. At low doping levels, the paramagnetic susceptibility of *trans*-$(N_yCH)_x$ remained practically constant, and differed little from that of non-doped *trans*-PA, but close to $y \simeq 0.05$ it increased sharply, accompanied by marked broadening of the EPR line and the appearance of temperature-independent χ_P. These data were interpreted[76] as proof of a first-order phase transformation at $y = y_c$ from a soliton lattice with zero density of states at the Fermi level $N(E_F)$ to a new quasi-metallic lattice, a "polaron metal", with a finite density $N(E_F)$. Such far-reaching conclusions appear doubtful, however, since there is insufficient information on the chemistry of the reactions in the PA–reducing agent system. Thus it has been established[77] that the solvation of Na^+ ions by THF has a marked influence on the width of the EPR line and the conductivity of specimens whose composition in the general case corresponds to the formula $[Na_y(THF)_z(CH)]_x$. At low values of y, solvation has a marked influence of σ, so that $\sigma_{z>0}/\sigma_{z=0} \simeq 10^4$, and with increase in y to 0.2, this ratio tends to 1; at low values of y for solvated Na^+ cations, $\Delta H < 1$ G, whereas for the non-solvated cations, $\Delta H \simeq 6$ G; at $y \simeq 0.01$, these ΔH values becomes equal.

Comparison of published conductivity and EPR data[77] also shows that there are strong interactions between the charge carriers and the local magnetic moments, that is the situation is analogous to that examined above for $(CHI_y)_x$; fairly strong spin–orbit scattering on the Na^+ ions should be expected. As a result, the paramagnetism of $(Na_yCH)_x$ should be determined by the simultaneous influence of several physical and chemical factors, among which the non-uniformity of the doping is of considerable importance. In Ref.76, the distribution of Na^+ was *a priori* regarded as uniform, but NMR data[78] show that even at y_{max}, the spectrum still contains a signal characteristic of non-doped PA.

In conclusion it may be noted that the absence of an EPR signal in the case of doped PA cannot be taken as evidence for the existence of spin-free solitons; for example, the same property is shown by chalcogenide and many other electrically conducting glasses.[38,75] In fact, the density $N(E_F)$ is most probably finite, but the electrons form pairs with antiparallel spins, so that the one-electron density of states $N(E_F)$ is equal to zero.

The reader interested in the detailed characteristics of non-crystalline solids is referred to published monographs.[38,75] It should be noted that the automatic transfer to disordered systems of ideas borrowed from classical band theory is not possible, and easily leads to artefacts.

V. OPTICAL PROPERTIES

The electronic absorption spectra of PA are completely typical of polyconjugated systems. The absorption bands of *cis*-PA has a clearly defined vibrational structure with maxima at 2.1, 2.3, and 2.4 eV, whose positions and intensities depend slightly on the previous history of the specimen. *cis–trans*-Isomerisation displaces the main maximum to 1.9 eV, and, as is often observed, to the disappearance of the vibrational structure.[79] By analogy with short polyenes, the absorption maximum can be assigned to a $\pi-\pi^*$ transition; the absorptivities, $\alpha \simeq 1.5 \times 10^5$ cm^{-1},[79] are characteristic of inter-band transitions in typical semiconductors.

After doping, the absorption band characteristic of the original PA becomes weaker, and is replaced by a new very broad structureless band at 0.5–0.9 eV. Typical results obtained by electrochemical doping[80] are shown in Fig.6. The absorption close to 0.7 eV is characteristic of all doped forms of PA, and is therefore associated with the electronic structure of the PA framework. Since the position of the new band corresponds approximately to the half-width of the band gap in the spectrum of the original PA, in the SSH model this band is called the "absorption in the middle of the gap". In addition, doping leads to the appearance in the infrared range of three strong bands at 0.17, 0.16, and 0.11 eV, whose positions are practically independent of the type of dopant, but are sensitive to the isotopic composition of the PA.[81]

The optical characteristics of PA have been discussed in detail.[19] It may be noted that in the SSH theory and its modifications, the spectrum of doped PA is determined by the characteristic vibrations of the charged solitons; the interaction of the solitons with π-electrons is accompanied by the appearance of new vibrational modes, three of which should be active in the infrared (IR) range. The IR absorption is described equally well by introducing topological defects of not the soliton type (C_{2v} symmetry) but the polaron type (C_{2h} symmetry). Particular attention has been paid to the absorption at about 0.7 eV, associated with the appearance of localised soliton levels exactly in the middle of the gap. Calculations[19] show that the appearance of a soliton in the PA chain should lead to the suppression of direct inter-band transitions, and the intensity of the transitions between the soliton levels should increase with increase in y as far as y_c, after which saturation should take place as a result of the overlap of these levels and the formation of a soliton band. The last conclusion, however, does not agree with experimental data,[33,36] according to which the optical density at 0.7 eV is proportional to the equilibrium concentration of the PA–dopant complex. The IR absorption data[82] also show a regular decrease in the transmission with increase in y as far as y_{max}.

The view that doping produces conjugation defects of different types is entirely reasonable. It is obvious, however, that the optical absorption can hardly be determined by the mobility of these defects; the broken bonds in three-dimensional inorganic amorphous semiconductors also give states situated "within the gap", but these states are not soliton states.[38] Thus the absorption spectra cannot serve as a test for solitons. A clear example is provided by a paper[83] whose authors reject completely the concept of conjugation defects, and attribute the "absorption within the gap" to charge transfer; a donor dopant adds an electron to the conductivity band, and an acceptor dopant generates a hole in the valence band. The conclusion that

there is alternation of the bonds in the PA chain is preserved completely, and the absorption is attributed to electromagnetic interactions between neighbouring chains. If however account is taken of the non-uniform distribution of the dopant, then the "absorption within the gap" can be directly related to an optical dielectric anomaly, characteristic of granulated metals. In this connection it may be noted that the maximum close to 0.7 eV, which is clearly defined in the reflectance spectra of $(CHI_y)_x$ films, disappears after the films have been compressed (unlike the other maxima in the IR range), and are replaced by a reflectance edge.[84] This phenomenon is readily explained in terms of the composite structure of doped PA using the familiar Maxwell–Harnett theory,§ but cannot be understood in terms of soliton models.

The charge-transfer model also provides an extremely effective interpretation of the three IR bands of doped PA; they are attributed to the interaction of the stretching vibrations of the framework with charge oscillations in a partly oxidised or reduced segment of the polymer; this is analogous to the situation for charge-transfer complexes based on TCNQ.[85] On the other hand, the IR spectra of β-carotene, which is an appropriate model compound with eleven conjugated bonds, are completely analogous to the spectrum of PA.[81,86] Thus published data[81,84–86] indicate that the optical absorption in PA is molecular in character. Quantum-chemical calculations of the electronic and vibrational structure[87,88] of model oligomeric radical-cations $C_{2n}H_{2n+2}^{+}$, cations $C_{2n+1}H_{2n+3}^{+}$, and dications $C_{2n}H_{1n+2}^{2+}$ [87,88] show that species of all three types are capable of contributing to the observed absorption. Moreover, the calculation[88] predicts intensive absorption close to 0.7 eV for β-carotene or PA doped with donors, with the formation of radical-anions $C_{2n}H_{2n+2}^{\cdot-}$; subsequent measurements[89] showed complete agreement with these predictions.

VI. PROBABLE MECHANISMS OF CONDUCTIVITY

An understanding of the mechanisms of charge transfer is hardly possible without taking account of the real structure of PA. The very complex morphology of PA was discussed above. Although the degree of crystallinity of the specimens reaches 80%, the average size of the crystallites is small, and does not exceed several nm.[90] The disorientation of the crystallites and the scatter in their sizes and shapes makes the direct determination of the crystal structure impossible; the diffraction patterns of PA seldom contain more than ten reflections, so that the crystallographic parameters have to be selected by a combined analysis of the diffraction patterns and calculations of the crystal packing.[25] The crystalline phase coexists with an amorphous phase; measurements of the thermo-stimulated creep[91] show that PA contains both amorphous volumes and thin inter-phase layers, separating the crystallites. It cannot be assumed that the general nature of the packing of the macromolecules in the amorphous phase differs significantly from that in the crystalline phase; the maxima of the diffuse scattering on the diffraction patterns coincide with the position of the principal reflection, but in the amorphous phase the concentration of packing defects (folds and twists in the chains, vacancies, etc.) is increased.

The diffraction patterns, however, are insensitive to local molecular defects, which to a large extent determine the charge transfer. The defects due to the presence in PA of sp^3-hybridised C atoms are particularly important. Acording to NMR and DPN data,[92,93] their concentration amounts to several percent. The presence of C(sp^3) atoms naturally breaks the conjugation chains. The Raman spectra, which provide a unique source of information on the magnitude of $N_{C=C}$,[94] show that, usually, not more than 20% of the chains have $N_{C=C} \geqslant 20$.

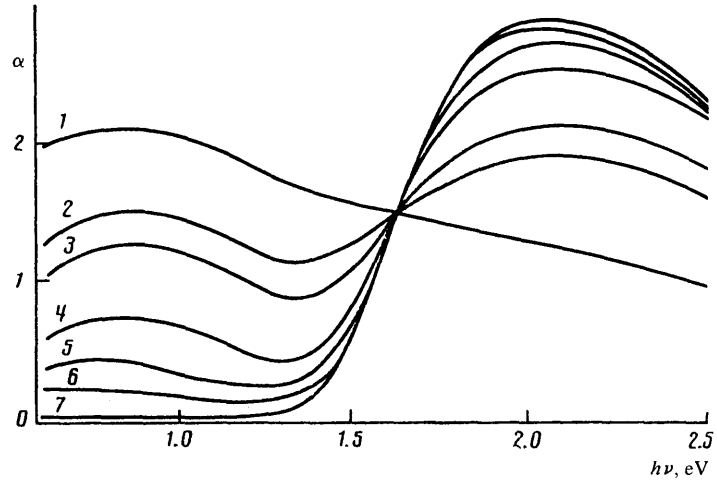
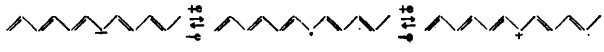


Figure 6. Absorption spectra of $[Ch(ClO_4)_y]_x$ at different levels of electrochemical doping[80] for y = 0.078 (*1*), 0.047 (*2*), 0.027 (*3*), 0.012 (*4*), 0.0065 (*5*), 0.003 (*6*), 0 (*7*).

§ See, for example, L.Genzel and U.Kreiberg, Z.Phys., 1980, **37**, 93.

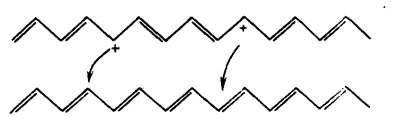
The macroscopic resistance of PA is apparently determined by a large number of factors (see section III). The indeterminacy associated with the disordered nature of the PA structure is so great that it is possible to construct only phenomenological models of charge transfer. When the real structure of PA is taken into account, it immediately becomes obvious that charged solitons or polarons cannot be responsible for the macroscopic conductivity; since they are topological conjugation defects, they can move only within the continuous conjugation segments. These segments are comparatively small, however, and the value of σ for doped PA is not related to the value of N_{C-C}; the electrical and magnetic properties of doped and non-doped PA are practically independent of the molecular mass in the range $400 \leqslant M_n \leqslant 920\,000$.[11] The results of studies of copolymers of acetylene with carbon monoxide,[95] where the mole fraction of CO was varied in the range 5–13%, are even more convincing. In these copolymers, the conjugation chain is frequently interrupted by $-C(=O)-$ units, so that $6 < N_{C-C} < 20$, yet the electrical properties of the doped and non-doped copolymers are the same as the corresponding properties of PA. The expected results were obtained from numerical calculations using the SSH model,[96] according to which the $-C(=O)-$ group in the *trans*-PA chain acts as a trap for neutral or negative solitons, and as a repulsion barrier for positive solitons.

For weakly doped ($y \lesssim 0.005$) *trans*-PA, Kivelson[97] proposed a mechanism of charge transfer by inter-soliton jumps. Every time a mobile soliton $S^{\cdot}$ passes close to a charged soliton $S^{\pm}$ which is bound by Coulombic attraction to an ion of the dopant and is therefore immobile, isoelectronic hopping of an electron to a neighbouring chain becomes possible:



Measurements of macroscopic characteristics, namely the frequency–temperature dependence of σ [98] and the $\sigma(T)$ relationships at different pressures,[99] agree well with the predictions,[97] but more detailed experiments on the influence of magnetic fields on the mobility of the carriers[100] gave results which contradicted the Kivelson model. In fact, the Kivelson mechanism is realistic only when the following requirements are satisfied simultaneously: 1) N_{C-C} should be very large, so that the solitons $S^{\cdot}$ can move along the chain without hindrance; 2) most of the chains should contain $S^{\cdot}$; and 3) the dopant should be distributed uniformly. From the previous sections it is clear that none of these requirements is in fact satisfied.

The corner-stone of the soliton concept is the assumption that the ground state of the chain is degenerate. The model of Ref.97 is obviously inapplicable in principle to either *cis*-PA or other conducting polymers. A different model[101] claiming to explain the mechanisms of conductivity in all doped polymers assumes interchain charge transfer by the correlated jumps of bipolarons:



The model of Ref.101 is designed primarily to explain spin-free charge transfer, and its experimental basis is the apparent absence of paramagnetism in doped PA. A semiquantitative calculation using this model reproduces only the general course of the $\sigma(y)$ relationship; so many assumptions, simplifications, and fitting parameters are used, however, that the agreement with experiment appears artificial. The greatest objections can be made to the actual idea of high-temperature jumps of bipolarons between the chains; by definition, the bipolarons in PA are not simply charged quasi-particles but topological defects in intramolecular chemical bonds. For this reason, the bipolaron model of Ref.101 can be regarded as an artefact, and its indvidual aspects will not be examined in detail.

It has been pointed out many times that the general character of the $\sigma(T)$ relationships for PA is similar to that of the typical relationships for doped inorganic amorphous semiconductors. This is why efforts are made to explain the electrical properties of PA using ideas based on jump mechanisms. For disordered systems, a unique role is played by $\sigma(T)$ measurements using alternating current. To ensure macroscopic conductivity using direct current or at low frequencies, the carriers must pass through the entire specimen; in a disordered system, this is possible only when there is a percolation network. At sufficiently high frequencies, percolation considerations are directly inapplicable, and the movement of the carriers reduces to jumps back and forward between two neighbouring localised states. This situation can be described by the so-called pair approximation.[75] A corresponding model for PA was proposed by Summerfield,[102], whose calculations adequately reproduce the static and frequency $\sigma(T)$ relationships, including the imaginary part of the complex conductivity, which is not consistent with the Kivelson model, and provide a qualitative description of the evolution of the density of states close to the Fermi level during doping. It should be emphasised that the Summerfield model does not contain assumptions about the nature of the states between which the jumps take place, in particular about their mobility, and at the same time reproduces the experimental data[98] more effectively than the Kivelson model.[97]

The electrical properties of moderately and highly doped PA are best described by the model of Sheng,[103] which was initially developed for granulated metals and which assumes the formation in PA of quasi-metallic clusters separated by narrow potential barriers—the non-doped PA regions. The movement of the carriers between the clusters takes place by tunnelling at low temperatures, and by thermally activated jumps at high temperatures. Thus detailed measurements[104] show a gradual decrease in the strength of the characteristic Mott relationship $\sigma \sim \exp(-T^{-1/4})$ when PA, moderately doped with AsF_5, is cooled to a temperature below 16 K; in the range $0.03\ K < T < 1\ K$, the conductivity of highly doped $[Ch(AsF_5)_{0.1}]_x$ becomes independent of temperature.[105] This behaviour cannot be explained without using tunnelling concepts.

Measurements of the temperature, field, and frequency dependence of the conductivity, and thermo-EMF measurements,[106] also show excellent agreement with Sheng's theory. The most convincing proof is apparently provided by the experiments of Refs.49 and 50 (see Fig.5); highly doped PA is in fact a system of non-combined quasi-metallic clusters. In this cluster model, the superposition of two main transfer mechanisms can be proposed. In one limiting case, the movement of the carriers is similar to the movement of the electrons in a metal, that is the interaction with the lattice is relatively weak, and the carriers have a high mobility and a comparatively long mean free path. In the other limiting case, the interaction with the lattice is strong, and the carriers have a very short mean free path and a low mobility. Within the clusters, the carriers probably move as a wave packet. Thus at a temperature below the Debye temperature, they may move as non-localised polarons of small radius in a narrow energy band, and at a temperature above the Debye temperature, the carriers move by jumps. This model is attractive, particularly since in polymers the Debye temperature is not strictly defined, and in fact there may be a distribution of Debye temperatures. Estimation of the drift mobility of the carriers μ, which is defined as the average rate of movement of the current carrier in the direction of the field and which is therefore a macroscopic characteristic, using the simple equation (3), gives for weakly doped PA the value $\mu = 5 \times 10^{-5}\ cm^2\ V^{-1}\ s^{-1}$.[39] As shown by Ioffe,[107] the average mean free path L of a carrier with an

effective mass m^* at ordinary temperatures is given by the expression $L \simeq 10^{-8}\ \mu(m^*/m_0)^{1/2}$, where m_0 is the mass of the free carrier. Assuming that the order of magnitude of the ratio m^*/m_0 is close to 1 gives for weakly doped PA the value $L \simeq 10^{-5}$ Å. This is many orders of magnitude smaller than the lattice constant a, so that the concepts of mean free path or mobility lose their significance. For highly doped PA, Eqn.(3) gives $\mu = 1\ cm^2\ V^{-1}\ s^{-1}$;[39] Ioffe's equation gives $L \simeq 1$ Å, which is also unlikely.

Dielectric measurements at high frequencies of $1.5-5\ cm^{-1}$ [108] revealed a high microscopic mobility (see Table), however, and it was concluded that the frequency dependence of the conductivity can be described by the superposition of two mechanisms. The first is due to free carriers, the absorption on which is described by the Drude relationship, and the second is associated with carrier jumps with the participation of phonons between microscopic states. At the microscopic level, these states are localised, so that the conductivity for direct and alternating current can be examined successfully using jump models.

Electrophysical characteristics of doped PA (accuracy of the determination ±25%).[108]

Specimen	n, cm^{-3}	τ, ps	μ, $cm^2\ V^{-1}\ s^{-1}$	σ, $\Omega^{-1}\ cm^{-1}$
trans-$(CHI_{0.011})_x$	$1.1\cdot10^{15}$	2.7	$3.7\cdot10^3$	0.5
trans-$[CH(AsF_5)_{0.011}]_x$	$5.0\cdot10^{15}$	10.0	$15.0\cdot10^3$	9.5

Notation: n and τ are the concentration and the mean free path of the current carriers μ the mobility of the carriers, and σ the specific conductance.

VII. THE STRUCTURE OF THE CONDUCTING PHASE

In a first approximation, doped PA can apparently be regarded as a composite containing two phases: non-doped and doped to saturation. In principle, depending on the previous history of the specimens, the volume fraction of the conducting phase can vary in the range $0 \leqslant f \leqslant 1$. The limiting cases correspond to the hypothetical single crystals, and in real specimens, some intermediate situation is established. This interpretation can be justified by the following experimental data.

1. In the absorption spectra there is an isosbestic point,[35,36,80] indicating the existence of only two states in PA–dopant systems, irrespective of the doping level (Fig.6).

2. Periodic recording of the diffraction patterns during doping always show a gradual decrease in the intensities of the reflections from the original PA, and the appearance of a new set of reflections. No signs of intermediate structures are detected.[109-111]

3. The reduced volume of the PA specimens is linearly dependent on the concentration of the dopant.[112]

Analysis of the experimental data indicates that the electron-conducting structures are formed first in the amorphous phase of PA. In fact, the first signs of the doped phase on the diffraction patterns appear only at $y \geqslant 0.02$; at $0 < y < 0.02$, only an increase in the intensity of the background scattering due to the adsorption of iodine on the PA surface was observed.[110] The swelling of the specimens during doping becomes appreciable only at $y \geqslant 0.05$.[112] The main increase in σ, however, takes place at $y \lesssim 10^{-2}$ (Fig.3). On doping with iodine from the gas phase, σ increases by five orders of magnitude in a time $t = 10^3$ s, and is saturated after $t = 10^4$ s, and both σ_{max} and the value of t at which it is reached are completely independent of the thickness of the PA films, which in the experiments of Ref.47 was varied from 5×10^{-6} cm to 10^{-2} cm.

At the same time it follows from kinetic data[47] that the diffusion of iodine in PA is very slow, with a coefficient $10^{-14}-10^{-13}\ cm^2\ s^{-1}$. Even for the small non-solvated Li^+ ion, the diffusion coefficient in PA is $\sim10^{-13}\ cm^2\ s^{-1}$ at 356 K.[113] These values are typical of solid-state diffusion. Thus the depth of the diffusion according to Fick's law $l_D = (2Dt)^{1/2}$ is ~0.1 μm at $t = 10^3$ s, which appears unlikely. It is known, however, that the diffusion coefficient along the grain boundaries in polycrystalline specimens is many times greater, and the activation energy of diffusion significantly lower, than in the volume of the granule. Moreover, it has been found[35,37] that the mass of the specimens in I_2 vapour increases rapidly at $t \leqslant 10$ s, and only at $10\ s < t < 10^4$ s, increases according to a t^n law, where $1/3 < n < 1/2$, indicating solid-state diffusion.

The combined data on the distribution profiles of the dopants and the kinetics of doping lead to the following picture. In the rapid first stage, the entire external surface of PA is covered with a monolayer of the dopant. In the slower second stage, the dopant diffuses into the amorphous phase, occupying the spaces between the crystallites. In the third stage, the dopant diffuses into the crystallites, and a new crystalline phase is formed. This picture is consistent with the morphology of PA and with the established $\sigma(y)$ relationships, without introducing doubtful assumptions about the uniform distribution of the dopant. The sharp increase in σ close to y_c (Fig.4) is naturally attributed to percolation, which takes place when the electrically conducting structures are formed in the space between the crystallites; the subsequent increase in f does not make a significant contribution to the macroscopic conductivity. In fact, the high conductivity is not determined by high crystallinity, since doping amorphous PA with iodine gives the same value of σ_{max} as doping highly crystalline specimens.[114]

The question of how the conducting phase of PA is "constructed" can be examined. The conductivity mechanisms which were examined above and which provide an adequate description of the electrical properties of PA are completely indifferent to the specific structure of the localised states or quasi-metallic clusters. There is apparently no particular need to assume that doped conjugated polymers differ fundamentally from the familiar low-molecular-weight charge-transfer complexes (CTC) of the TTF–TCNQ type.[2] In the last case, before the formation of the CTC, the electron clouds of the donor and the acceptor are closed, and when the molecular crystal is formed, extensive charge transfer takes place, converting the crystal to the quasi-metallic state; the initially completely full band becomes half-filled. It may be said that in this case, TCNQ is "doped" by TTF or vice versa, so that the concepts of "dopant" and "matrix" can be interchanged.

From this viewpoint, doped PA represents a particular case of systems of the TTF–TCNQ type with a low and varying concentration of donor or acceptor molecules. The optimum magnitude of the charge transfer is 0.5–0.8 e.[115] This is possible either with partial charge transfer or when a CTC with stoichiometry different from 1:1 is formed. In PA, both situations are probably realised; the first may be characteristic of chemical doping, and the second of electrochemical doping, when the dopant is only a source of counterions preserving the electrical neutrality of PA. The role of donors or acceptors in PA is played by conjugated segments of varying length, bounded by defects in the molecular structure.

The basic principle of supermolecular organisation, ensuring high conductivity, is well known; it is necessary to have a non-stratified bifilar type of packing, where the donors and acceptors crystallise in regular isolated stacks, within which mixed valence states are produced, and the movement of the carriers takes place by a so-called

relay mechanism.[2] The individual details of this mechanism as applied to conducting polymers have been discussed by Wegner.[116] Two models of the packing in doped PA have now been developed on the basis of the diffraction patterns and calculations. The first model [25] assumes structural analogies with intercalated graphite; the acceptor molecules are introduced between the close-packed planes of PA. In the resulting layer structures, the transfer of the carriers should take place chiefly within the partly oxidised planes of PA, and should be quasi-two-dimensional in character. It is noteworthy that this model is unsuitable for interpreting the diffraction patterns of PA doped with alkali metals. For these complexes, a quasi-one-dimensional structure is assumed, in which the metal ions occupy channels in the tetragonal lattice formed by four parallel PA chains.[25] If the analogy with graphite is retained, however, there are no grounds for expecting such significant differences between the structures of the various complexes.

On the other hand, it follows even from a previous analysis[110] that the diffraction patterns for $(CHI_y)_x$ are consistent not only with the intercalation model. In an alternative model, the dopant is introduced between PA layers in which the planes of the macromolecules are arranged normal or almost normal to the plane of the layer. The relationship between the two models is illustrated schematically in Fig.7. The analogy between the second model[110,116] and the packing of low-molecular-weight CTC and radical-ion salts of TCNQ is obvious. The most convincing evidence in support of this type of packing was recently obtained in a diffraction analysis of highly oriented films of *trans*-$[CH(SbF_6)_y]_x$.[116] The crystal structure can be represented as the superposition of two incommensurable sub-lattices: the first is formed by the PA chains, and the second by the SbF_6^- ions. The second lattice is hexagonal and disordered along the crystallographic direction coinciding with the axes of the PA macromolecules. The distance between neighbouring PA segments forming the stacks is 3.44 Å, which ensures effective interaction between the π-electrons. In this model, the PA segments reduced or oxidised to radical-ions are stabilised by complex formation with neighbouring neutral segments according to the scheme

$$(CH)_n^{\pm\cdot} + (CH)_n \rightleftarrows [(CH)_n(CH)_n]^{\pm\cdot}$$

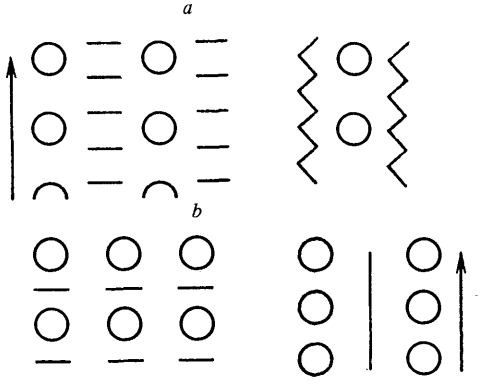


Figure 7. Probable crystal packing in doped PA (on the left—projection along the PA chain direction, on the right—projection at right angles to the PA chain direction): *a*) quasi-one-dimensional model,[116] *b*) quasi-two-dimensional model;[25] the arrows show the preferred direction of charge transfer; the circles represent the dopant, and the dashes the end faces of the planar PA chains.

It follows directly from this scheme that the complex formation is possible not only in the crystalline phase but in all cases where a minimum of two PA segments are arranged relative to one another in such a way that charge transfer is possible between them. These complexes are apparently acceptable as the prototype of the localised states; their concentration increases with increases in y, and they merge at any $y = y_c$. It is appropriate to recall that the packing of the macromolecules in the amorphous phase differs little from that in the crystallites. According to the appropriate comparison made in Ref.117, the local structure of the rigid-chain polymers is more like the packing of raw spaghetti in a partly filled box than the packing of cooked spaghetti in a pan. This makes clear the importance in amorphous polymers of the intermolecular interactions which stabilise the quasi-metallic state and which make possible the existence of conducting clusters of appreciable dimensions.

The "metallic character" of the clusters, revealed by the different slopes of the curves in Fig.5, is variable, and depends on the dopant. In "physical" soliton models, dopants of the same type (for example acceptors) are not distinguished. For chemists, the different electrophysical properties of PA—dopant complexes can be attributed to the difference in the degree of charge transfer and the difference in the stability constants of the CTC (see section III). The most stable complexes are probably formed in the reaction of PA with AsF_5, which is a very strong Lewis acid. The correctness of these arguments is apparently confirmed by the data of Ref.108, given in the Table.

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From the extensive range of fundamental problems relating to PA, as before, the question of the nature of the conductivity is attracting the greatest attention. There arises the question of whether solitons (or polarons) are physically real, or merely an elegant but artificial method of description. The answer to this question is important not only for theoreticians. The development of new materials of practical importance can hardly be achieved without a detailed understanding of the electronic processes responsible for their properties. A complete understanding has obviously not yet been reached. The chemistry and physics of macromolecular "synthetic metals", of which PA is the prototype, still appear as a mosaic, and considerable efforts are required to establish a clear and consistent picture.

Nevertheless, the information which has already accumulated up to the present provides some possibilities for generalisation. According to the familiar Occam's principle, entities are not to be multiplied beyond necessity. In accordance with this principle, the present authors consider that the principal properties of PA and its analogues can be examined using more traditional non-soliton approaches. The soliton concept, however, has provided an exceptionally effective stimulus for theoretical and experimental studies which might not have been carried out in a different situation. This has led to a better understanding of the entire set of relationships between the structure and properties of matter—one of the cardinal problems of present-day chemistry.[118]

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The Glass Points and Dielectric Relaxation of Carboxyl-containing Copolymers and Ionomers Based on Them

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The influence of the content and distribution of carboxy-groups along the polymer chain, the amount and nature of the cations introduced, and the dielectric constant of the polymer matrix on the dielectric relaxation and the glass points of carboxyl-containing copolymers (CCC) and their ionomers is considered. It is shown that the specific features of the properties of the ionomers are determined by the formation of ionic aggregates: multiplets in the presence of a low content of ion clusters at a fairly high concentration of ions which depends on the structure of the initial copolymer. It is concluded that the type of distribution of the carboxy-groups and the dielectric constant of the polymer matrix have a decisive influence on the ion aggregation process.
The bibliography includes 85 references.

CONTENTS

I. Introduction 475
II. Contribution of hydrogen bonds to the intermolecular interaction of carboxyl-containing copolymers 475
III. Dielectric relaxation properties of certain carboxyl-containing copolymers 476
IV. Transition to the vitreous state in ionomers 477
V. Dielectric relaxation of ionomers 479

I. INTRODUCTION

The partial or complete neutralisation of the COOH groups in carboxyl-containing copolymers leads to the occurrence of ionic interactions, which imparts to the copolymers unique properties capable of being varied within wide limits.[1-4] In the majority of ionic copolymers, this interaction of the ions entails microphase separation caused by the incompatibility of the salt groups and the hydrocarbon units of the chain.[5] At a certain concentration of the ions, the phase separation leads to the coexistence of two types of ionic aggregates, namely multiplets and clusters.

The introduction of ions into polymers is reflected most notably in the rheological behaviour of the melts, the relaxation of stresses, the dynamic, mechanical, and dielectric properties, and the glass point.[6-12] The present reivew deals with questions concerning the dielectric relaxation and glass points of ionomers based on carboxyl-containing copolymers of different composition and structure. Thermomechanical and dielectric studies make it possible to obtain information about the molecular mobility and the character of the aggregation of the salt groups and about the influence of this aggregation on important technological characteristics of the ionomers.

II. CONTRIBUTION OF HYDROGEN BONDS TO THE INTERMOLECULAR INTERACTION IN CARBOXYL-CONTAINING COPOLYMERS

The properties of polymers containing carboxy-groups are determined to a large extent by their ability to form hydrogen bonds between the C-OH groups. In contrast to chemical cross-links, hydrogen bonds are unstable, dissociating and reforming anew under the influence of thermal motion. However, it is in fact the hydrogen bonds that have a decisive influence on the mechanism of the vitrification of polymers[13] and on their mechanical properties in the highly elastic and viscofluid states.[14]

The majority of the carboxy-groups in carboxyl-containing copolymers are linked by hydrogen bonds into dimeric complexes[15-17] whose heat of dissociation varies from 7 to 15 kcal mol^{-1},[18-21] which agrees well with data for low-molecular-weight carboxylic acids.

Spectroscopic studies make it possible to characterise quantitatively the formation of hydrogen bonds from the temperature variation of the absorption band maxima corresponding to the $\nu(C=O)$ vibrations of the free COOH groups and dimeric associated species (1740-1750 and 1695-1705 cm^{-1} respectively).[22-26] On heating to the glass point T_g, the relative intensities of these bands hardly change, while at higher temperatures the low-frequency band weakens and the intensity of the 1740 cm^{-1} band increases.[18,22] For the styrene-methacrylic acid (MAA) (85:15) copolymers, an inflection associated with the dissociation of the intermolecular hydrogen bonds appears on the curves for the temperature variation of the 1700 and 1745 cm^{-1} absorption band intensities at 120 °C, which corresponds to the glass point, also found to be 120 °C by other methods.[18,27]

Detailed study of the temperature variation of the intermolecular interaction energy in polystyrene (PS) and in the styrene-MAA copolymer (16 mole %) by differential IR spectroscopy[28,29] showed that appreciable disruption of the hydrogen bonds and weakening of the van der Waals intermolecular interaction (interaction mainly between benzene rings) begin already in the region of the temperature of the β-transition;† the first stage of this process occurs in the range of the glass points. The character of the temperature variation of the energy for intermolecular bonds of different types is different. Relatively weak van der Waals interaction changes stepwise, falling especially sharply after the attainment of the fluidity temperature. In the case of hydrogen bonds, the temperature variation of the energy shows breaks at characteristic temperatures.[28]

The main effect occurring when carboxy-groups are introduced into the copolymer—the formation of hydrogen bonds—intensifies the intermolecular interaction. However, the copolymerisation of styrene with MAA entails also a series of other effects: a weakening of the van der Waals interaction, an increase in mechanical losses in the region of the β-transition compared with PS; an increase in the

†The β-transition, which corresponds to the onset of the movement of short sequences of styrene units, is a precursor of the movement which occurs at T_g.[30,31]

degree of coiling of the chains.[29] It follows from the study of the conformational changes in the styrene–MAA copolymer that these effects are especially pronounced, starting from an MAA concentration of 10–15 mole %, in the copolymers, and the average distances between the hydrogen bond bridges become comparable to the increase in the size of Kuhn's kinetic segment in PS.[29]

In view of the small decrease in the intermolecular interaction energy on transition through the glass point,[28] the appreciable change in the mechanical properties of polymers in the region of T_g cannot be explained solely by the decrease in intermolecular interaction energy and is apparently induced by the appearance of cooperative segmental motion. This is confirmed by the shift of T_g towards higher temperatures with increase in the content of COOH groups in the copolymer. Thus the increase in the MAA content in the copolymer with methyl methacrylate (MMA) from zero to 15 and 28% is accompanied by an increase in the glass point from 103 °C to 109° and 137 °C respectively.[17] The shift of T_g towards higher temperatures with increase in the number of carboxy-groups is caused by the increased hydrogen bond network. In the butadiene–MAA copolymer, the increase in the number of hydrogen bonds with increase in the content of the acid also increases the dynamic modulus of elasticity and T_g.[32] The dependence of T_g on the content of the acid component is described most satisfactorily by the equation for cross-links.[20,32]

The majority of the experimental data lead to the conclusion that interchain cross-links are formed preferentially via hydrogen bonding.[15,18,23] The change in the thermodynamic parameters in the ethyl methacrylate–MAA copolymers with increase in the MAA content is also explained by the intensification of the interchain interaction as a consequence of the formation of hydrogen bonds:[33] a decrease in their heat capacity, entropy, and free energy and an increase in the equilibrium constant and the limiting copolymerisation temperature, which corresponds to an increase in the thermodynamic stability of the copolymers. The above changes in the thermodynamic parameters of the copolymers are much greater than might have been expected from the additivity of the properties of the copolymers relative to the corresponding homopolymers.

The intramolecular bonds probably begin to appear in the presence of a fairly high content of carboxy-groups. In a study[34] of the physicomechanical properties of MAA and butyl acrylate copolymers, a maximum was observed on the curves for the dependence of the stability on composition. The presence of the maximum has been explained by the fact that initially an increase in the MAA content entails an increase in the number of intermolecular hydrogen bonds and hence the stability of the copolymer increases. On further increase in the MAA fraction in the copolymer, intramolecular bonds begin to appear, which leads to the coiling of the macromolecules into globules; as a result, the stability of the copolymer diminishes owing to the decrease in the energy of cohesion. In polyacrylic acid, dimerisation takes place mainly via the carboxy-groups belonging to the same hydrocarbon chain.[35]

III. DIELECTRIC RELAXATION PROPERTIES OF CERTAIN CARBOXYL-CONTAINING COPOLYMERS

The study of the dielectric properties of CCC provides important information about the role of hydrogen bonds in molecular relaxation proceses. The results of the investigation of the dielectric relaxation processes in copolymers of ethylene with methacrylic and acrylic acids have shown that α- and β-relaxation processes predominate in these copolymers.[36,40] The relaxation α-transition is associated with vitrification processes in the copolymer. The number of dipoles participating in the α-process can be calculated from the experimental data by the Onsager equation

$$N = \frac{9kT}{4\pi\mu^2} \frac{(2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_0 - \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + 2)^2}$$

where N is the number of dipoles, T the absolute temperature, μ the electric dipole moment of the COOH groups amounting to 1.75 D,[37] and ε_0 and ε_∞ are the relaxation and non-relaxation dielectric constants respectively. The number of free COOH groups determines the intensity of the observed α-relaxation. The α-process is in fact associated with their mobility and reorientation in the external electric field.[38,39] The low-temperature β-process is determined in both copolymers by the low mobility of the main chains of the copolymer.[36]

The β-relaxation observed in the copolymers of MAA and the polar methyl methacrylate at temperatures below T_g is essentially due to the movement of the ester side groups.[41] This is confirmed by the finding that any change in the MAA content does not shift the β-relaxation peak along the temperature axis (Fig.1), while the intensity of the dielectric relaxation $\Delta\varepsilon_\beta$ diminishes linearly with increase in the MAA fraction in the copolymer. The activation energy for the β-process has been estimated as 19 kcal mol^{-1}.[41] The sharp peak in the region of high temperatures (Fig.1) corresponds to the α-process, which is determined by the segmental thermal motion of the chain. With increase in the MAA content in the specimen, the temperature at which α-relaxation is observed shifts towards higher values and at the same time the activation energy for the α-process increases, which means that the segmental motion of the main chain of the copolymer is limited by the MAA units.

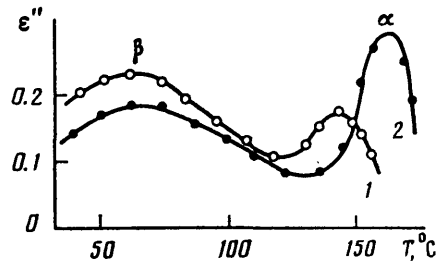


Figure 1. Temperature variation of the dielectric losses coefficient ε'' for the MMA–MAA copolymers at 30 Hz; MAA content (mole %): 1) 15; 2) 28.[41]

For the α-process, the increase in the relaxation intensity with temperature is caused by the increase in the number of mobile units as a result of the dissociation of the hydrogen bonds and the number of mobile units is assumed to be proportional to the dissociation constant. The dissociation energy of the hydrogen-bonded MAA dimer in the highly elastic state has been determined from the temperature variation of the relaxation intensity for α-processes ($\Delta\varepsilon_\alpha$). It proved to be 13 kcal mol^{-1}, which agrees with the dissociation energy determined from IR studies[17] for the MAA dimer in the MMA–MAA copolymer and with data for the dimers of other acids. However, the dissociation energy of the dimeric complex in the vitreous state is much lower than in the highly elastic state (0.7 kcal mol^{-1}). This has been attributed to differences between the supermolecular structures of the vitreous and highly elastic states. Although it follows from IR studies that the most intense

dissociation of hydrogen bonds occurs in the highly elastic state, a large number of the hydrogen-bonded dimeric complexes remain stable even at temperatures above T_g, as shown by the low value of the dissociation constant (4.27×10^{-5} mol cm^{-3}) and by the character of the dependence of the dielectric relaxation intensity on the number of cross-links.[17] Hence it follows that, even in the highly elastic state of the CCC, the hydrogen bonds act as fluctuating intermolecular bonds, although their energy is lower by a factor of 10 than the energy of covalent cross-links.

The replacement of methacrylic acid by acrylic acid (AA), i.e. the absence of α-methyl groups, influences the molecular mobility of the MMA–AA copolymer. In the study of the dielectric properties of these copolymers, two relaxation transitions were also observed: the high-temperature α-transition associated with segmental mobility and the low-temperature β-transition due to the mobility of the side groups.[42] In the case of the α-process, the relaxation intensity $\Delta\varepsilon$, calculated from the area under the curve describing the variation of the dielectric losses coefficient ε'' with $1/T$ in accordance with the Williams equation, increases with increase in temperature (in contrast to the methacrylate homopolymer for which $\Delta\varepsilon$ is almost independent of temperature). The dissociation energy of the AA dimers, determined from the temperature variation of $\Delta\varepsilon$, agrees well with the calculation based on the IR spectra. The activation energy ΔH^* and the temperature of the maximum T_{max} for the α-process decrease with increase in the content of the AA dimer in contrast to the MMA–MAA copolymer, for which both ΔH^* and T_{max} increase with increase in the MAA fraction.[41] On the other hand, the dissociation constants of the dimers of both copolymers, found from the IR spectra, are the same. Evidently, in the absence of the α-methyl group, the acrylic fragments play an important role in the increased segmental mobility in the copolymer at temperatures exceeding the glass point when the AA dimers decompose. The characteristics of the β-process depend little on the AA content, as in the case of the MMA–MAA copolymer.

In the case of the styrene–MAA copolymer,[43] a single peak, whose position and height increase with increase in the MAA content, is observed in the temperature variation of the dielectric losses coefficient ε'' in the region of the glass point. This is associated with the fact that an increase in the MAA fraction in the copolymer increases the number of cross-links formed by the acid dimers, which increase T_g and hence shift the α-relaxation to the region of higher temperatures. Calculations based on the monomer–dimer equilibrium have shown that 20% of the COOH groups are in a free state at T_g; they in fact contribute to ε''. With increase in temperature, the dimers $\rightleftarrows$ free COOH groups equilibrium is displaced to the right. Therefore, the higher the temperature corresponding to the ε'' peak, the greater its intensity. The initial sharp rise on the curve describing the variation of the temperature of the α-relaxation maximum ε'' with the content of carboxy-groups[43] is explained by the fact that, at low concentrations of the dimeric complexes, cross-links can suppress molecular motion more effectively that at high concentrations. This is also indicated by the minimal electrical conductivity σ (COOH groups make the main contribution to σ) at a concentration of 5 mole %, which is associated with the influence on σ not only by the properties of the charge carriers but also by the molecular mobility of the polymer matrix.

In the styrene–MAA block copolymers (with an MAA content of 5–30 mole %), two clear-cut α-processes are observed: at ~130 °C (α_1) and at 180 °C (α_2). The presence of two maxima, corresponding to the α-processes, not only confirms the block structure of the copolymers synthesised in emulsion but also indicates their microheterogeneity, i.e. the existence of two phases in the specimen.[44] One phase contains predominanatly polystyrene (PS) blocks and the other is enriched in poly-MAA blocks. The α_1-process at 130 °C is associated with the manifestation of segmental mobility of the PS blocks and its position depends only slightly on the ratio of the monomer units in the copolymer. The α_2-process at 180 °C is due to the molecular mobility in the region of the phase containing the poly-MAA blocks. With increase in the MAA content in the copolymer, the α_2-process shifts somewhat towards high temperatures and its intensity increases.

Thus the properties of CCC are mainly determined by their ability to form hydrogen bonds. Additional contacts at the intramolecular and intermolecular levels arise as a result of the hydrogen bonds, which increases the glass points and fluidity of the CCC. At low temperatures, the carboxy-groups exhibit a tendency to dimerise via hydrogen bonding, which renders them dielectrically inactive. With increase in temperature, the hydrogen-bonded carboxy-groups dissociate and exert the corresponding influence on the dielectric relaxation, for the behaviour of which free COOH groups are responsible.

IV. TRANSITION TO THE VITREOUS STATE IN IONOMERS

A partial or complete neutralisation of the carboxy-groups in the CCC leads to the appearance of a series of their specific properties, which are similar for different classes of ionomers. Thus the ability to adsorb water, the character of the variation of T_g with the concentration of ions, and the mechanical and dielectric properties of ethylenic and stryrene ionomers are very similar, while polystyrene and polyethylene differ markedly,[45] which is due to the characteristic features of the structures of the ionomers determined by the manifestation of ionic interactions.[46–53]

Neutralisation of carboxy-groups in CCC influences especially the glass point, which increases after the introduction of ionised groups into the polymer.[54–65] This increase in T_g is associated mainly with the decrease in segmental mobility as a consequence of ionic interactions and therefore depends on the nature of the cation.[5] Analysis of T_g data from the standpoint of the anion–cation interaction as a factor limiting segmental mobility led to the following general T_g relation[57] for fully neutralised silicates, phosphates, and acrylates:

$$T_g = Aq/a + B$$

where q is the charge on the cation, a the distance between the centres of the charges on the anion and the cation, and A and B are constants. Graphically the dependence of T_g on q/a for both polyphosphates and other fully ionised homopolymers is represented by straight lines having the same slope.[66] In partially neutralised polyphosphates T_g also varies linearly with q/a, but partly neutralised acrylate systems do not exhibit such a dependence. This may be caused by the presence of highly structured rigid associated species, which appreciably diminish the segmental mobility of the polymer.

In organic ionomers, a linear dependence of T_g on q/a is in general not observed, because the morphology of these materials is fairly complex and may vary with the concentration of ions. When the content of ions in the ionomers is low, the initial increase in T_g with the concentration of ions is in most cases linear (from 2 to 10 K per mole % of the ion-containing comonomer).[5,67,68] The glass points of sodium ionomers based on ethylene[69] obey satisfactorily the equation

$$T_g = n_1 T_{g1} + n_2 T_{g2},$$

where n_1 and n_2 are the mole fractions and T_{g1} and T_{g2} are the glass points of the two homopolymers. The study of different mechanisms of the increase in T_g for styrene ionomers[19] leads to the conclusion that the main mechanism of the rise of T_g in these ionomers involves the formation of cross-links between ionic domains and not a copolymerisation effect, as in ethylenic ionomers.[69] It is most likely that the regular increase in T_g with the concentration of ions

in both ionomers is caused by a superposition of two effects: the cross-linking and copolymerisation mechanisms with the influence of one of these mechanisms predominating in each type of ionomer.

The monotonic variation of T_g with the ion content of ethylenic ionomers and also the results obtained in the study of the relaxation of stresses, the absorption of water, and the dynamic, mechanical, and dielectric properties show that ionic aggregates are present in these ionomers even at very low concentrations of the ionic comonomer.[70] On the other hand, the study of the character of the variation of the glass points and of the fluidity of the ionomers based on styrene (20 mole % MAA) over a wide ion concentration range[65] reveals the breakdown of the linear dependence of the transition temperatures on the ion concentration for 30% neutralisation (~6 mole %).

Such breakdown of the monotonic variation with increase in the content of sodium methacrylate above 6 mole % has been observed for all the parameters of the styrene-based ionomers;[71] this is a result of the change in the morphology of the ionic aggregates, namely the transition from small multiplet formations to higher-order ionic accumulations—clusters. The existence of clusters is due to the equilibrium between the electrostatic forces arising between individual multiplets‡ and the elastic forces of the macromolecular chains, which resist the attraction of the multiplets.[72] One of the necessary conditions for the formation of clusters is that the interactions of the hydrocarbon chains with one another and with ions should be different,[73] which ensures an effective attraction between the ions and tends to stabilise the clusters. High ion concentrations and low dielectric constants of the polymer matrix are also necessary for the formation of clusters; on heating above a critical temperature, the clusters decompose.[73]

The unusual dependence of T_g on the content of the acrylic acid salt in ethyl acrylate copolymers is also associated with the formation of ionic clusters.[5,56] A single general curve is obtained for all the ions investigated (Na^+, Cs^+, Li^+, K^+, Ca^{2+}, Ba^{2+}) when the function $T_g = f(Cq/a)$ is plotted. Here C is the content of salt groups, q the charge on the cation, and a the distance between the centres of the charges on the anion and cation (Fig.2). The non-linear section corresponds to the deviation from the principle of the temperature–time superposition in the relaxation of stress for the ethyle acrylate–sodium acrylate copolymer (12 mole % of the ion-containing comonomer) and reflects the formation of clusters. Evidently in the region of low values of Cq/a, to which corresponds the linear section of the curve, the multiplets exert the dominant influence, while the clusters determine the behaviour of the ethyl acrylate ionomers for higher values of Cq/a. It follows from the data of Matsuura and Eisenberg[56] that the "cluster formation" principle, determining the rheological behaviour of ionomers, depends both on the ion concentration and on q/a; the character of the dependence of T_g on q/a, illustrated in Fig.2, is encountered only in materials in which fairly intense cluster formation takes place.[5] The effect involving the increase in T_g almost by a factor of two when the ion content in ethyl acrylate ionomers varies from 10 to 25% can be understood if it is supposed that the clusters ensure a more effective cross-linking than simple multiplets.

An important factor influencing T_g for ionomers is the amount of water which they have absorbed; water, whose content increases with ion concentration, lowers T_g. It has been shown that T_g for the sodium salt of polyacrylic acid decreases by ~8 K each time the water content is raised by 10%.[66] In ethyl acrylate-based ionomers in the presence of a definite amount of water (≥20 wt.%), T_g varies linearly with the water content regardless of the ion concentration (in the region of 20–50 mole % of sodium acrylate).

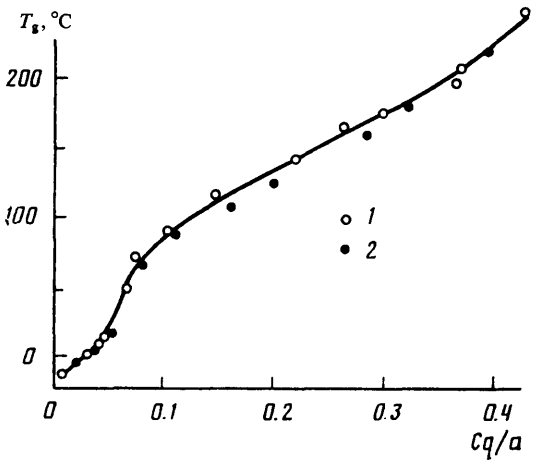


Figure 2. Dependence of T_g for ionomers based on the ethyl acrylate–acrylic acid copolymer on Cq/a for different ions: 1) Na^+, Li^+, Ca^{2+}, and Ba^{2+}; 2) K^+ and Cs^+.[56]

These data are qualitatively similar to the attainment of a plateau on the plot of T_g against ion concentration, which is observed for ionomers based on styrene–n-butyl methacrylate copolymers.[74] The glass points of these ionomers increase with increase in the ion content to 1.5 mole %. The limiting value of T_g is higher by 5–20 K that the T_g for the initial copolymer and depends on the molecular weight of the copolymer. The plateau on the relation between T_g and ion concentration can be accounted for by the balance between the influence of the ions, which increases the rigidity of the chain, and the plasticising action of water. In ionomers based on copolymers of acrylic acid and methyl methacrylate, T_g increases with increase in ion concentration in the range $0-1.5 \times 10^{-3}$ equiv. cm^{-3}.[75] Above the critical concentration (1.5×10^{-3} equiv. cm^{-3}), which is independent of the content of acrylic acid in the initial copolymer, T_g does not change. This can be explained by the for-mation of clusters of ionised groups which do not influence T_g. It has been suggested by Matsuura and Eisenberg[56] that the contradictions between the results of their studies of T_g for ethyl acrylate-based ionomers and the data of Tsutsui et al.[75] may be due to a number of causes. It may be that the character of the dependence of T_g on the ion content in these ionomers reflects the differences between the structures of the copolymers or clusters. Furthermore, the high degree of conversion of ionomers based on MMA–AA copolymers (36.5–48.7%), which is much higher than the degree of conversion of ethyl acrylate ionomers (7.2–14.5%), may lead to a high compositional inhomogeneity in the polymer and as a consequence to the separation of the specimen into different phases. Another possible cause of the disagreements is the presence of water, remaining in the specimens investigated by Tsutsui et al. after drying under mild conditions, which decreases T_g.

The nature of the cation should evidently exert an appreciable influence on the T_g of the ionomers via the parameter q/a. It follows from the study of a series of ionic copolymers based on butadiene that the univalent cations Na^+ and Li^+ have a greater influence on T_g than the univalent anion I^-.[76,77] There are indications

‡Multiplets are small compact ionic aggregates.

that Mg^{2+} ions in the ionised ethylene–acrylic acid copolymers are more effective from the standpoint of the increase in T_g than Na^+ ions. The dependence of the glass point and fluidity of the ionomers on the nature of the cation introduced can be traced satisfactorily in ionomers based on statistical styrene–methacrylic acid (20 mole %) copolymers.[64]

Under identical neutralisation conditions, the glass points and fluidities of the ionomers containing Na^+ ions exceed the corresponding values for the copolymers neutralised by Rb^+ ions.[64]. The reason is apparently that, as a result of the aggregtion of the salt groups of the ionomers in the hydrocarbon matrix, there is a possibility of a distribution of the ionised carboxy-groups in which they find themselves opposite one another, so that an electrostatic interaction takes place between them. If account is taken of the fact that the strength of interaction between ions is inversely proportional to the distance between them, which is determined by the radii of the ions, then "ionic cross-linking" with the Na^+ cation, which has a greater radius than the Rb^+ cation, is more stable. For this reason, specimens of ionomers containing Na^+ have higher transition temperatures than the corresponding Rb^+.

Another picture is observed if bivalent metal acetates have been used for the neutralisation of the carboxy-groups of the styrene–MAA statistical copolymer. Neutralisation by Zn^{2+} and Ca^{2+} ions alters very slightly the glass points and fluidities of the ionomers. This phenomenon can be explained by the fact that the neutralising agents in this case are not the doubly charged metal ions M^{2+} but singly charged ions of the type $M(CH_3COO)^+$ formed via the reaction[78]

$$M(CH_3COO)_2 \rightleftarrows M(CH_3COO)^+ + CH_3COO^-$$

The acetate groups in such singly charged ions shield the ionic charges by virtue of their large size, diminishing thereby the stability of the ionic cross-linking, i.e. they manifest a kind of plasticising effect. This is confirmed by the finding that the thermomechanical curves for ionomers with different contents of both Zn^{2+} and Ca^{2+} are identical and exhibit all the temperature-dependent transitions characteristic of thermoplastics. Furthermore, ionomers with 30% substitution by Ca^{2+} and Zn^{2+} ions are readily soluble in dioxan and dimethylformamide, which also confirms the absence of "cross-links".[64]

For the same content of salt groups, the mode of their distribution along the copolymer chain has a great influence on the glass points of ionomers.[64,65] Thus, whereas in statistical styrene–methacrylic acid copolymers a complex type of dependence of T_g on the ion concentration is observed, the introduction of MAA into the polystyrene chain in the form of a block leads to the absence of such dependence of T_g on the degree of neutralisation. This is caused by the characteristic features of the structure of these polymers: the ionomers formed are block copolymers having the composition (MA-Na–MAA)–(styrene–MAA–MA-Na)$_m$. Statistical copolymers are formed within the limits of the blocks and the distribution of the monomers in them is as follows: in the first block, there is more sodium methacrylate (MA-Na) than methacrylic acid, while in the second block the styrene–MAA content greatly exceeds the content of sodium methacrylate. Since the size of the styrene–MAA–MA-Na blocks is comparable to the size of the kinetic segment, ionic cross-links have little influence on T_g,[65] which is confirmed by the insignificant displacement of the maximum of the tangent of the dielectric losses angle for the α_1-process towards higher temperatures with increase in the degree of neutralisation.

The properties of ionomers based on graft copolymers are determined by the length of the blocks containing the ionogenic groups. They are similar to those of the ionomers of block-copolymers provided that the chain length of the grafted polyacid is sufficiently large. Thus the thermomechanical curves for ionomers based on graft ethylene–maleic anhydride copolymers,[64] in which the length of the side sections containing carboxy-groups is fairly considerable, showed the appearance of additional transition temperatures due to the manifestiation of the presence of ionic cross-links; these temperatures depend on the content of the acid and the degree of its neutralisation. The T_g for the monomers investigated are independent of the degree of neutralisation and are close to the melting point of polyethylene (100 °C). However, if the sections of the grafted polyacids are short (several monomer units), then the variation of the glass point with ion concentration in the ionomers of graft copolymers will resemble that for the ionomers of statistical copolymers. Such behaviour has been observed for ionomers based on graft styrene–MAA copolymers in which the short chains of the grafted poly-MAA are distributed statistically along the polystyrene chain.[44]

Thus the mode of distribution of the carboxy-groups (statistical block and graft copolymers) leads to different types of aggregation of the salt groups in the corresponding ionomers, which is distinctly manifested by the behaviour of the T_g of the ionomers. However, ion aggregation is difficult in a medium with a high dielectric constant,[5,73] which is reflected by the absence of a dependence of T_g for such ionomers (ionomers based on MAA–MAA copolymers) on the nature and amount of the cations and by the weak dependence of the maximum in the tangent of the dielectric losses angle for α-relaxation on the degree of neutralisation.

V. DIELECTRIC RELAXATION OF IONOMERS

The neutralisation of the carboxy-groups in the CCC alters the dielectric relaxation of the copolymers, owing to its sensitivity to the presence of the polar groups of acids and salts directly involved in the formation of clusters. Dielectric studies can yield valuable information about the structure and character of the molecular motion of ionomers.[40,43,55,79–84]

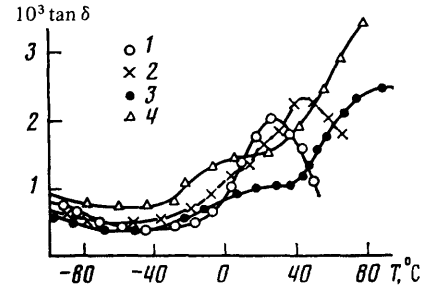


Figure 3. Temperature variation of tan δ for the sodium salts of the ethylene–MAA copolymer (4.1 mole %) at 1 kHz; degree of neutralisation (%): 1) 0; 2) 19; 3) 41; 4) 72.[79]

The intensity of α-relaxation in ethylene–MAA copolymers diminishes with increase in the extent of neutralisation and α_1- and α_2-relaxations appear (Fig.3).[79] The α_1-relaxation is associated with the T_g of the ionic phase of the ionomer; this is confirmed by the absence of α_1-relaxation in the copolymer and by the increase in its intensity and its shift towards higher temperatures with increase in the degree of neutralisation and by the bend in the curve describing the frequency and temperature variation for the α_1-process. The bend in the frequency-temperature variation for the α_2-process shows that this relaxation characterises the T_g of the hydrocarbon phase,

which becomes dielectrically active by virtue of the presence of free carboxy- or salt groups linked to the segments of this phase. The water absorbed by the ionomers shifts the α_1-peak towards lower temperatures, which is associated with the plasticising effect of water on the ionic phase. At a temperature of about –43 °C, an additional peak appears, whose height is approximately proportional to the water content and whose position depends slightly on its amount.[79] Modern calculations of the relaxation intensity have shown that the mobility of the water molecules themselves is responsible for this peak.

In the sodium salts of the ethylene–acrylic acid copolymer (9.3 mole %), the temperature of the α-relaxation maximum does not change and the height of the peak increases with increase in the degree of neutralisation W to 20%; for $W > 30\%$, the temperature of the α-maximum rises and the height of the peak diminishes following the appearance of α_1-relaxation.[40] Simultaneously with the change in the character of the temperature variation of the maximum and height of the relaxation peak as a function of the degree of neutralisation, the character of the temperature variation of the relaxation time also changes: for low extents of neutralisation, it is described by the Williams–Lundell–Ferry equation, whilst for high extents of neutralisation it is described by the Arrhenius equation. The dielectric increment $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, calculated from the Cole–Cole diagram for the α-relaxation, increases in proportion to the degree of neutralisation up to 20% ($\Delta\varepsilon = 0.119$ for $W = 0$ and 0.826 for $W = 20\%$), diminishing rapidly with increase in the degree of neutralisation above 30%. The influence of the degree of neutralisation on all the relaxation properties of the ethylene–AA copolymer indicated can be explained by the formation of ionic clusters for $W > 30\%$.[40] Since Δε at 30% neutralisation is higher than for the copolymer, it is concluded that not all the COONa groups are combined into clusters and it is suggested that these groups are dielectrically active in the α-relaxation process.

Detailed study of β-relaxation has thrown defnite light on the investigation of the structure and molecular motion in ionomers, because its extent is associated with the polar COONa groups which have not entered the clusters. Indeed, for the sodium salts of the copolymer, the position of the β-peak along the temperature scale is independent of the degree of neutralisation W, but the peak height increases with increase in W.[40,57] The dielectric increment for β-relaxation increases in proportion to the degree of neutralisation up to 20% and diminishes for $W > 30\%$. Since at low ion concentrations aggregation is not observed, the number of polar COONa groups responsible for β-relaxation increases with increase in the ion content. As a result of the formation of ionic clusters at a higher ion concentration, the number of polar groups involved in β-relaxation diminishes. Consequently the dielectric β-relaxation provides new evidence for the existence of clusters in ionomers.

The formation of ionic aggregates in copper(II) salts of the ethylene–acrylic acid copolymer proceeds with more difficulty than in the sodium salts owing to the complex structure of the copper(II) salts.[84] The temperature dependence of the dielectric losses coefficient ε″ for the copper salt of the ethylene–AA copolymer, which has in the main the dimeric structure of hydrated copper acetate,[85] is characterised by two maxima located at 50 °C (α-relaxation) and –100 °C (β-relaxation) for 20% neutralisation. The first maximum is due to the molecular Brownian movement at temperatures above T_g and the second is associated with the local molecular mobility below T_g, as in the sodium salts of these copolymers. In the region of α-relaxation the temperature T_{max}, corresponding to the maximum value of ε″, increases with increased extent of neutralisation and a diminution of ε″ is observed simultaneously up to $W = 34\%$. The α-relaxation process at $W = 71\%$ has a complex character and consists of α_2-relaxation at 0°C and α_1-relaxation at 60 °C. The dependence of the logarithm of the frequency of the ε″ maximum on $1/T_{max}$ satisfies the Williams–Lundell–Ferry equation for $W < 5\%$ and the Arrhenius equation for $W > 20\%$,[84] which indicates the retardation of the Brownian movement as a consequence of the interaction of the ionic groups with increase in the extent of neutralisation from 5 to 20%. The dependence of the dilelectric increment Δε on the extent of neutralisation passes through a maximum at $W = 5\%$, but at $W > 20\%$ the quantity Δε gradually diminishes, while T_{max} increases, owing to the onset of ionic aggregation at $W > 20\%$ (Fig.4). The increase in Δε and the decrease in T_{max} in the specimen neutralised to the extent of 71% indicate that, in the highly neutralised polymer, many Cu^{2+} ions can remain outside the ionic aggregates. This has also been observed for β-relaxation. The α_2-relaxation, appearing in the 71% neutralised specimen, refers, according to the authors,[84] to the molecular motion of short segments, incorporating copper(II) salts, between ionic aggregates. This is confirmed by the low activation energy for α_2-relaxation (~ 18 kcal mol^{-1}).[84]

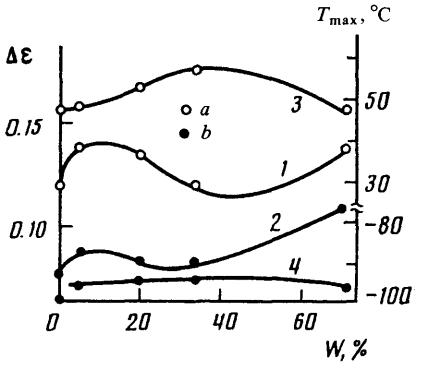


Figure 4. Dependence of the dielectric increment Δε (curves *1* and *2*) and of the position of the relaxation maximum T_{max} (curves *3* and *4*) on the degree of neutralisation W for the α- and β-relaxation in the copper(II) salts of the ethylene–AA copolymer (9 mole %): *a*) α-relaxation; *b*) β-relaxation.[84]

α_2-Relaxation has also been observed in the copper(II) salts of the styrene–methacrylic acid copolymer.[84,85] These salts have three types of structure: I—monomeric, II—monohydrated copper acetate, and III—pseudo-anhydrous copper formate, the fraction of each depending on the method used to prepare the copper carboxylate. These structures influence the molecular motion of the polymer; however, ionic aggregation in all the copper(II) salts of the styrene–MAA copolymer could not be observed either by the low-angle X-ray diffraction method or by electron microscopy.

Ionic aggregation with formation of clusters occurs in ionomers based on styrene with MA-Na (fully neutralised specimens containing between 2 and 9 mole % of sodium methacrylate).[80] The temperature variation of the tangent of the dielectric losses angle (tan δ) shows, after the subtraction of the losses due to conduction, two readily distinguishable overlapping maxima for all the ion concentrations except 2 mole %. Both peaks shift towards high temperatures with increase in the ion content. The low-temperature peak is due to regions with a low ion concentration, while the high-temperature peak is associated with large aggregates which have a higher T_g. The overall area under the peaks for the variation of tan δ with the reciprocal of temperature is correlated very satisfactorily with the overall ion concentration in the ionomers (correlation coefficient

0.975). The area under the low-temperature peak (α_2-relaxation) increases with increase in the salt content up to 5 mole % and then remains constant at higher concentrations.[5,57] This is evidence for the saturation of the hydrocarbon matrix by ionic groups at this ion concentration; at the higher ion concentration, all the additional ions are combined into clusters. On the other hand, the area under the high-temperature peak (α_1-relaxation) increases continuously with increasing concentration of the salt groups; at an ion concentration >5 mole %, the increase accelerates.

With increase in temperature, the concentration of ionic groups in the hydrocarbon phase grows at the expense of the ion-rich region, i.e. the clusters decompose at high temperatures. This is indicated by the change in the relative sizes of the two relaxation peaks with increase in frequency. When the frequency is raised, which shifts both relaxation peaks towards higher temperatures, the height of the α_2-peak increases compared with the high-temperature α_1-peak.[57,80]

Thus it follows from the dielectric studies of the fully neutralised sodium ionomers based on the styrene–MAA copolymer[80] that clusters and multiplets coexist starting with an ion concentration of 2 mole %; the hydrocarbon matrix is saturated by ionic groups at 5–6 mole % of sodium methacrylate; the clusters dissociate at elevated temperatures. In the partly neutralised styrene–MAA polymers (9 mole %) two dielectric relaxation peaks appear at relatively low degrees of neutralisation (starting with 25%) in the region of the transition to the vitreous state, indicating the simultaneous presence of both multiplets and clusters in the ionomers.[43]

The temperature of the maximum T_{max} and the intensity ($T\Delta\varepsilon$) of the peak depend on the degree of neutralisation (Fig.5). Both peaks shift towards higher temperatures with increase in the extent of neutralisation W. However, at $W > 65\%$ (which corresponds to 5.85 mole % of the salt in the ionomer)[43] the increase in the extent of neutralisation leads to a faster shift of T_{max} for the high-temperature peak; on the other hand, T_{max} for the low-temperature peak increases very slowly, which is due to the saturation effect. Thus, as in fully neutralised styrene–MAA copolymers, in the partly neutralised copolymers containing ~6 mole % of ions the matrix is saturated by multiplets, while on further increase in the ion concentration the ionic groups begin to combine into clusters.

In the fully neutralised polymers, only 2% of the COO^-Na^+ groups are in a "free" state (are present as simple ion pairs), while in the remaining polymers they are combined into multiplets or clusters.[43] The presence of COO groups in partly neutralised copolymers increases the degree of dissolution of salt groups in the polymer matrix, such groups becoming dielectrically active.

While T_{max} for the low-temperature α_2-peak of the partly neutralised polymer is appreciably higher than for the pure salt containing the same number of ionic groups, in the case of the high-temperature peak the opposite situation obtains. Furthermore, the intensity of the α_2-peak of the partly neutralised polymer is much greater than that of the peak of the pure salt. The higher intensity of the low-temperature peak of the partly neutralised polymer is associated with the fact that the COONa groups combine with the COOH groups. Apart from giving rise to a considerable number of small clusters in the partly neutralised specimens (the clusters in the pure salt are more stable and larger), these additional interactions suppress the molecular motion in the matrix and shift the α_2-peak relative to the pure salt.

The different modes of distribution of the MAA units in the statistical block and graft copolymers lead to different characters of the aggregation of the salt groups in the corresponding monomers, which is clearly manifested in dielectric relaxation.[44] For the statistical styrene–MAA copolymers, the qualitative changes in the temperature variation of $\tan\delta$ for the sodium, rubidium, zinc, and cadmium ionomers with increase in the degree of neutralisation take place in the same manner. For all the ionomers, the intensity of the α-process increases with increase in the degree of neutralisation, which can be explained by the increase in dipole moment as the carboxy-groups are neutralised. The shift of the α-process to the high-temperature region is associated with the restriction of the segmental mobility with increase in the degree of neutralisation owing to ionic interactions. The high-temperature $\tan\delta$ maximum (above 200 °C) corresponding to molecular mobility in ionic clusters, whose presence might have been expected on the basis of earlier data,[43,80] could not be observed either because of the low fluidity temperatures of the ionomers investigated (below 200 °C) or as a consequence of the large dielectric losses associated with the increase in the electrical conductivity of the material in the region of the transition to the viscofluid state.

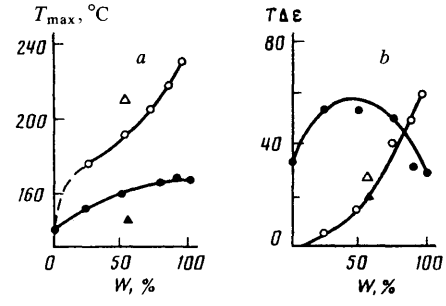


Figure 5. Dependence of T_{max} (*a*) and $\Delta\varepsilon$ (*b*) on the degree of neutralisation W for the high-temperature (1) and low-temperature (2) relaxation in the partly neutralised styrene–MAA copolymer (9 mole %); 3) and 4) the values of T_{max} and $T\Delta\varepsilon$ for the high- and low-temperature dielectric relaxation maxima respectively for the fully neutralised copolymer containing 5.06 mole % of the salt.[43] [The numbering of the symbols was omitted from the figure in the Russian text (Ed. of Translation).]

For the ionomers based on the styrene–MAA block copolymers, two distinct α-relaxation processes are observed, which makes it possible to infer their microheterogeneity.[44] The α_1-process is associated with the segmental mobility of the styrene–MAA–MA–Na blocks, while the α_2-process is determined by the segmental mobility of the phase enriched in MA–Na. With increase in the degree of neutralisation, the maxima in the tangent of the dielectric loss angle for the α_1- and α_2-processes become more intense, the α_2-process shifting markedly towards high temperatures (Fig.6). The small displacement of the process agrees with the small increase in the softening temperatures of the ionomers. The increasing intensity of the α_1-process shows that the PS blocks in these block copolymers do indeed contain statistically distributed MA–Na units which have a high dipole moment. The blocks enriched in MA–Na are segregated into a separate phase. The shift of the α_2-process to the temperature range above 250–300 °C (with a corresponding shift of the fluidity temperature) indicates intense ionic interactions within sections of this phase. Evidently the sizes of these sections are such that they incorporate blocks ranging from several macromolecules.

Therefore the viscous flow of the ionomer can begin only at a temperature where the energy of thermal motion is sufficient to dissociate the intermolecular ionic bonds to "deinhibit" the molecular mobility in these sections.

For the ionomers based on graft styrene–MAA copolymers, a single peak corresponding to the α-process is observed in the temperature variation of tan δ; its position and intensity vary with increasing degree of neutralisation similarly to the peak for the α-process involving ionomers based on statistical copolymers. Such similarity of the properties of the ionomers of graft and statistical copolymers shows that the short chains of graft poly-MAA [44] are distributed statistically along the chain of the PS macromolecule.

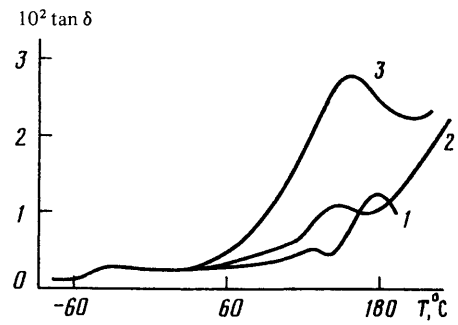


Figure 6. Temperature variation of tan δ for the styrene–MAA block copolymers (12 mole %) (curve *1*) and of its sodium ionomers (curves *2* and *3*); degree of neutralisation (mole %): 2) 10; 3) 40.[44]

Thus the dielectric behaviour of the ionomers can be most convincingly interpreted from the standpoint of microphase separation: whereas there is only one peak of the dielectric losses angle tangent for the initial copolymer, after neutralisation two such peaks with a fairly high intensity appear. This phenomenon reflects the existence of two glass points. The first of these is the T_g of the matrix, which contains a small amount of ionic groups, while the second is the T_g of the phase-separated ion-rich region. In other words, below a certain ion concentration the dielectric behaviour of the polymers is determined by small compact ionic aggregates (multiplets), which behave like cross-links, while above this critical concentration the larger ionic aggregates (clusters) influence the properties of the ionomers.

The dielectric relaxation and the character of the variation of T_g with ion concentrations for monomers based on vitreous and partly crystalline CCC are qualitatively similar despite the differences between the stabilities of the main chains and the dielectric constants of the hydrocarbon matrices. The nature of the neutralised groups determines the capacity of the salt groups for aggregation and therefore influences the physical properties of the ionomers. The mode of distribution of the salt groups along the polymer chain and the dielectric constant of the polymer matrix have a decisive influence on the aggregation of ions. The nature of the cation and its content influence the properties of the ionomers at specific concentrations of the carboxy-groups, which depend on the structure (type) of the initial copolymer.

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Problems in the Physical Chemistry of Membrane Processes

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The new problems of modern industry can be solved only on the basis of fundamentally new technologies, materials, and energy sources. Among the new chemical technologies, a unique position is occupied by membrane technology. Membrane processes may find extensive application in practically all spheres of human activity. Membrane technology is already demonstrating its technical and economic advantages in a number of large-scale production processes. Approximately one quarter of the world production of desalinated water, reaching about 10 million cubic metres per day, is now obtained by membrane technology. The use of electrodialysis with ion-selective membranes for water treatment in modern thermal power engineering enables the country to save annually more than 300 thousand tons of sulphuric acid, 250 thousand tons of alkali, and 5 thousand tons of ion-exchange resins, and to reduce by more than 600 thousand tons the annual discharge of mineral salts into water systems.

The change to membrane electrolysis in the production of caustic soda and chlorine makes it possible not only to intensify considerably the large-scale production of these materials and to reduce the energy required, but also to ensure the production of highly pure alkali, and hence to avoid the use of mercury electrolysis, which at present is one of the principal sources of mercury contamination of the environment. The introduction of a membrane separation unit in the production of a number of chemical products using hydrogen (the synthesis of ammonia and methanol, the oxo-synthesis, hydrocracking, and hydro-desulphurisation) gives a significant increase in productivity and decrease in energy consumption. The use of membranes to control the composition of the gaseous medium in fruit- and vegetable-storage chambers makes it possible to increase the storage times of agricultural products by 2–8 months with no loss of quality.

The possibilities provided by membrane technology have not been fully explored. The operational parameters of membranes depend on many factors, including the thermal and chemical stability of the starting materials, and the conditions of their transformation and modification. The membranes acquire a definite structure, whose characteristics determine the specific nature of the transfer of ions and molecules through the membranes. Thus the production of highly effective membranes for a definite purpose is associated with a range of varied problems in physical chemistry and materials science, the solution of which requires fundamental studies of the structure and functional properties of the membranes. It is necessary to introduce into research practice modern methods which make it possible to control the structure and other characteristics of the materials at all stages of the preparation and modification of the membranes. At present, unfortunately, these studies are hindered by the lack of the appropriate equipment in research centres.

The advantages of membrane technology can be fully realised only with the optimum organisation of the membrane processes, requiring the selection of sound separation schemes, membrane apparatus parameters, and working conditions. The problems associated with the optimisation of membrane processes must be

solved using appropriate mathematical models containing phenomenological parameters characterising the properties of the membrane system. The selection of these parameters should also be based on the results of physicochemical studies of membrane separation processes with allowance for the change in the functional properties of the membranes during use.

The solution of this entire range of physicochemical and materials-science problems is necessary for the formulation of the integral concept of the development of membrane technology and the choice of its most effective applications. The complex character of the problems arising requires the coordination of effort in the organisation of planned scientific research and the establishment of a membrane technology, including the development of monomers, fibres, films, and fabrics for reinforcing membranes, and of thermally and chemically stable adhesives for membrane elements used for different purposes. In the Soviet Union at present this coordination is carried out by the MNTK (Inter-branch Scientific and Technical Complex) "Membrany" (Membranes), which combines the forces of more than thirty plants, institutes, and laboratories of the Ministry of the Chemical Industry, the Academy of Sciences of the USSR, the Ministry of Higher Education, and other departments.

The programmes of fundamental research work which have now been developed have been designed primarily to solve general theoretical problems associated with the determination of the nature of the selectivity of the transfer of components in membranes of different type, the development of the scientific principles of the synthesis of new polymeric materials, and the production of membranes based on them. Promising possibilities are provided by the synthesis of inorganic materials of new types for membranes, characterised by higher ionic conductivity values and a high thermal stability, which is extremely important for the production of membrane systems combining separating properties with other functional properties (for example catalytic). As yet, insufficient attention is being paid to these questions. At the same time, recent achievements, particularly in the production of ceramics with several functions (including special electrical properties), indicate the promising possibilities provided by this search.

Of the specific new types of membrane whose development it is extremely important to complete, mention may be made of the following: ion-exchange membranes (cation-exchange, anion-exchange, bipolar), stable to reactive media and high temperatures (up to 80 °C); perfluorinated membranes with different functional groups for membrane electrolysis and various special purposes; thermally and chemically stable membranes for reverse osmosis; highly selective membranes for separating carbon dioxide, ammonia, sulphur-containing gases, helium, oxygen, and other components from gas mixtures; composite membranes with high permeability for haemofiltration; microfiltration membranes for purifying highly reactive liquids in the chemical, biological, and other industries, capable of being used at temperatures up to 150 °C; and highly effective liquid and quasi-liquid (impregnated liquid) membranes for extracting required components from natural and industrial solutions.

In view of the promising possibilities provided by their development, it is necessary to search for biofunctional membranes with catalytic, energy-transforming, and information-transforming properties by immobilising fragments of biological systems on synthetic supports.

The papers in the present collection reflect some of these directions in the development of fundamental studies of the physical chemistry of the processes involved in the membrane separation of liquid and gas mixtures. In addition to the examination of the general regular features of the transport of ions and molecules through membranes with different functions, the characteristics of the membrane processes of gas separation, reverse osmosis, ultrafiltration, and electrodialysis have been analysed. The problems associated with the development of new membrane materials and the production of membranes, and problems of membrane biocatalysis, have also been discussed.

The development of the scientific principles of the technology of membranes of different types and the physicochemical principles of the processes involved in membrane separation is making it possible to develop and introduce into practice various membrane processes for separating liquid and gas mixtures and obtaining new substances, and also membrane catalytic processes.

In the technical and economic validation of new technologies, including membrane technology, it is necessary to adopt a comprehensive approach involving without fail an adequate analysis of all the advantages of the new technologies, including allowance for the effects of the technological processes on the environment, estimation of the effect of the loss of various substances discharged in industrial effluents, and allowance for the cost of water. Ecological factors may be very important, since new technologies should produce little or no waste products, practically eliminating the loss of valuable components and reducing considerably the harmful influence of industrial products on the enviroment.

All this means that new economic thinking is required to raise technology to a new level. Scientist-economists, when carrying out a comprehensive technical and economic analysis of the change to new technological processes, must not simply fix the existing state of affairs, but must look ahead and see the future. Only comprehensive technical and economic validation with calculation of the economic effect can open the road to the new technologies and enable them to be introduced.

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From Biological to Synthetic Membranes

S.F.Timashev

The main principles of the functioning of transport systems in biological membranes and especially of processes involving the selective transport of ions and molecules in synthetic membranes (ion-exchange, gas separating, reverse osmosis, ultrafiltration, membranes, etc.) are examined. It is shown that, under the conditions of intense mass and electromass transfer, the transport of ions and molecules in synthetic membranes acquires features characteristic of transport processes in biological membranes both as regards the organisation of the transport (transport via channels) and in terms of the principal kinetic features. The prospects for further research into the physical chemistry of membrane separation processes and processes leading to the formation of new substances, including membrane catalysis, are discussed.
The bibliography includes 115 references.

CONTENTS

I. Introduction 487
II. Characteristic features of ion and molecule transport processes in biological membranes 487
III. The nature of the selective transport of components in synthetic membranes 489
IV. Membrane catalysis 498
V. Conclusions 500

I. INTRODUCTION

Membrane technology is faced by major and large-scale problems whose solution requires the creation of new membrane materials and membranes of different types with effective functional characteristics (permeability, selectivity with respect to the target component, combination of catalytic and separating properties) and also a change-over to intensive mass and electromass transfer conditions in membrane systems (increase in current density, high effective pressure, the use of external influences). This necessitates not only a profound knowledge of the physical chemistry of the membrane separation, the characteristic features of ion and molecule transport processes in synthetic (organic, inorganic) membranes, but also the understanding of the main principles of the functioning of the most effective membrane systems in living nature. The heuristic value of the latter knowledge can be hardly overestimated. In the first place, this is a source of new ideas and concepts concerning the ways of increasing the selectivity of the transport of charged and neutral species, the most effective methods for the intensification of transport processes, the detailed mechanisms of the recording and transfer of information, and the methods for the transformation and utilisation of energy of external sources in a wide variety of processes.

However, in order that these ideas should acquire a pragmatic shape, it is essential to make them available to a wide range of specialists engaged in problems of the physical chemistry of membrane separation and problems concerning the creation of new materials and membranes based on them. This is particularly necessary, since studies on transport processes in native systems and synthetic membranes are prosecuted by different scientific groups almost independently. This article is one of the first attempts at the realisation of this important programme (see also the authors previous communications[1,2]).

II. CHARACTERISTIC FEATURES OF ION AND MOLECULE TRANSPORT PROCESSES IN BIOLOGICAL MEMBRANES

The cells of a living organism include a wide variety of types of membranes and membrane structures[3]—surface membranes (cell or plasmatic membranes) and a multiplicity of intracellular membranes. The surface membranes fulfill important barrier functions maintaining the internal autonomy of the cells and protecting them from the entry of foreign substances. Enzyme transport systems, using the energy stored in the organism and ensuring the supply to the cell and the removal from the latter of different components which makes it possible to maintain the required concentrations of the necessary substances within the cells and in their organelles, function simultaneously in the surface membranes.

Biological membranes consist of lipids and proteins. It has been established that there exist several hundreds of types of membrane lipids. More than half of them (up to 90%) are double layer forming phospho- and glyco-lipids, which manifest pronounced diphilic properties, i.e. they can be divided in space into polar and non-polar parts (the latter consist of hydrocarbon chains).

Under physiological conditions, the double layers are in a liquid crystal state and the description of their molecular organisation must therefore include the dynamic aspect apart from the structural (geometrical) aspect. The lipid double layer is illustrated schematically in Fig.1.[4] An important element of this model comprises the regions in the sublayer *a* in which short-range order ("cluster") is retained, their characteristic transverse dimension amounting to 0.8 nm. They incorporate up to 40–60 hydrocarbon chains (20–30 phospholipid molecules). The molecular packing in the clusters is fairly close to the crystal packing and is "more compact" than in the isotropic region *i* of the double layer.

The clusters are dynamic formations with a lifetime of $\sim 10^{-7}$ s. They are continuously decomposed and reformed, migrating along the double layer. The movement of the lipid fragments in the cluster should then occur simultaneously, i.e. it should represent a cooperative process. The boundary regions between such migrating clusters can be regarded as dynamic defects in the double layer.

In biological membranes, the complex dynamic system of the lipid double layer described includes a large number of protein molecules having different dimensions and shapes. In particular, proteins occupy 35% of the surface of the membrane in erythrocytes. The structural organisation of the phospholipids in the regions corresponding to binding to the protein can then change significantly, so that one may speak of the existence of protein–lipid complexes. The hydrocarbon chains of the phospholipids exist under native

conditions in a quasi-liquid state, the effective viscosity of the double layer amounting to ~5 P at 20 °C and this is why the protein molecules are capable of migrating along the membrane. The "liquid-mosaic" model of the structure of the membranes proposed by Singler and Nicholson has played a major role in the abandonment of the view that lipids constitute a simple structural partition.[3] If one imagines a section through the membrane in the plane perpendicular to its surface, then the proteins incorporated in the membrane double layer must produce a mosaic pattern. Such mosaic model of the membrane, presupposing the existence under native conditions of both double layer sections and regions constituting protein–lipid complexes, is the most attractive.

The distribution of various components (both proteins and lipids) in the membrane is asymmetric for functional reasons. The lateral mobility of the protein fragment in the double layer permits the formation of the most varied structures with a non-uniform (highly non-equilibrium) redistribution of components in the membrane. These can be lipid–lipid and protein–lipid clusters, protein–lipid domains differing in the composition of the proteins and lipids from other regions of the membrane, and domains comprising components within the membrane formed as a result of the binding of the latter to physiologically active compounds distributed on the surface of the membrane. The appearance of such complex metastable formations in biological membranes, which are thermodynamically open systems and exchange matter and energy with the environment, greatly expands the functional possibilities of cell structures.

In order to understand the principal characteristic features of the complex transformations occurring in the transport systems of biological membranes during their functioning, we shall consider the principles of the action of bacterial rhodopsin or bacteriorhodopsin (BR)—the simplest of the transport systems in which photodependent proton transport takes place and a proton electrochemical potential gradient $\Delta\mu_{H^+}$—the macroergy of biological systems according to Metchell's chemo-osmotic hypothesis[5]— is established on the cell membrane. Bacteriorhodopsin is the sole protein component of the purple membranes (PM) ("end-plate") of halobacteria, containing retinal as the chromophoric group, which forms a Schiff base with the protein component of the molecule—opsin BR consists of 248 aminoacid residues.

The attempts to establish the disposition of the protein in the lipid layer were based on the hypothesis that the hydrophobic sections of the polypeptide chain of the molecule should be disposed in the inner hydrocarbon region of the membrane, while the hydrophilic sections should be exposed to the aqueous phase. A scheme for the disposition of BR within the PM in the form of a sequence of seven α-helical blocks passing through the lipid double layer follows from these ideas.[6] The use of computers in order to select the α-helical structures having the lowest energies led to the conclusion[7] that each of the seven α-helical segments contains between 28 and 32 aminoacid residues and that pairs of charged groups form salt bridges within the membrane or are distributed on its surface.

Apart from the absorption in the region of 280 nm, typical for proteins, the BR spectrum is characterised by a broad absorption maximum at a wavelength $\lambda_{max} \simeq 560-570$ nm and a minor band near 400 nm. Continuous illumination of BR with white light shifts λ_{max} in the "light–dark" difference spectrum to the region of 412 nm. The state corresponding to $\lambda_{max} \simeq 412$ nm is stabilised in salt solutions or on lowering the temperature; in the dark, this state relaxes thermally to the initial state. The study of the kinetics of the formation and decomposition of the product absorbing at $\lambda_{max} \simeq 412$ nm by flash photolysis demonstrated the presence of intermediates, which precedes the formation of the product absorbing in the short-wavelength region, and also of a series of subsequent adducts. It has been suggested that the intermediate states be specified in the alphabetical order using the letter subscripts to λ_{max} in the differential optical spectrum.

The schematic photocycle obtained by Lozier et al.[8] is illustrated in Fig.2, which indicates the half-lives of the intermediates at room temperature under physiological conditions. The photochemical process is only the first stage–the formation of the intermediate K which takes place over a period of ~10 ps. This is followed by spontaneous thermally induced transitions between the states, such transitions being increasingly retarded in each succeeding stage. In particular, the activation energy for the K → L transition proved to be 0.5 eV and that for the L → M and M → BR transitions was found to be 0.7 eV. Later measurements[9] in the temperature range from 160 to 300 K yielded 0.68 eV for the activation energy for the

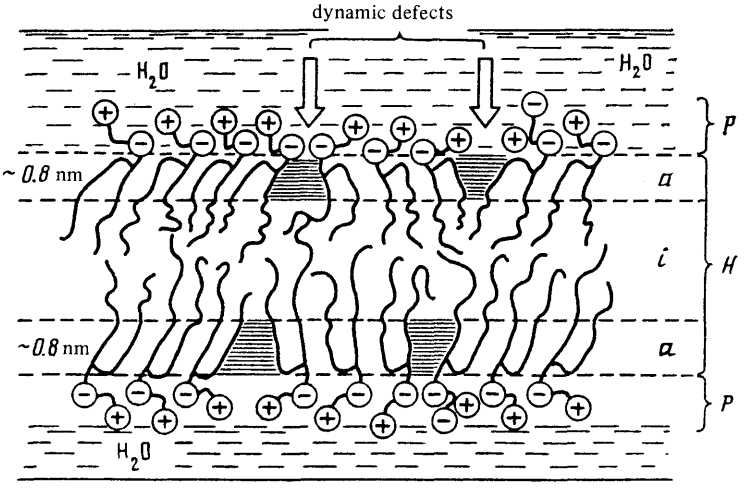


Figure 1. Schematic illustration of the structural organisation of the lipid double layer: *P*–the region of polar groups; *H*–the region of hydrocarbon chains; *a*–"anisotropic" region; *i*–"isotropic" region.[4]

K → L and L → M transitions. The lower rate of the L → M process is caused by the reduced entropy of activation in this stage.

The time of the total turnover of the BR photocycle is 0.01 s under physiological conditions and can increase by several orders of magnitude when the conditions are changed (the temperature and humidity are reduced and certain chemical compounds are present). The O_{640} and N_{530} intermediates cannot always be detected reliably, because the O state is very sensitive to external conditions, for example, to the pH of the medium. The existence of the N intermediate is indicated merely by the presence of the corresponding shoulder on the differential optical spectra. The primary process in the photocycle—the formation of the K_{630} state—takes place under the influence of light even at helium temperatures (2–9 K). A decrease in temperature shifts λ_{max} towards longer wavelengths.

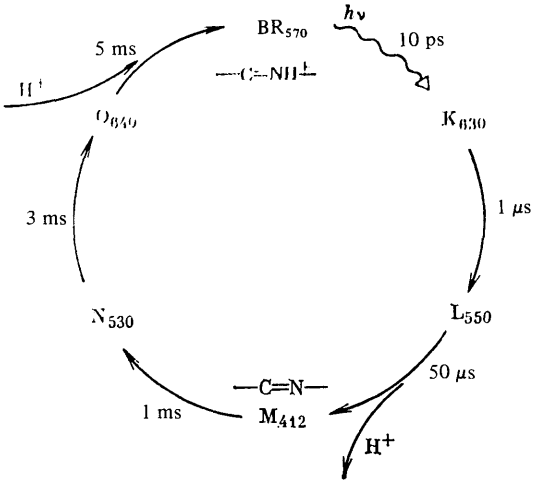


Figure 2. Schematic representation of the photocycle of bacteriorhodopsin[7] (the approximate time of formation of the first intermediate—the batho-intermediate K—and the half-lives of the subsequent intermediates L, M, N, and O are indicated; the subscripts denote the absorption band maxima of the corresponding intermediates in nanometers).

The discussion of the complex processes occurring in this surprising photodependent system and in other transport enzymes is outside the framework of this review (for further details about them, see, for example, Stoeckenius et al.[9]). The corresponding analysis made it possible to formulate appropriately the main principles of the functioning of transport systems in biological membranes.[1,2,10,11]

1. The transport of ions and molecules is determined by the submicrostrucure of the membrane and takes place via submicrochannels—specialised (ionic channels in excited membranes and transport ATPases) or arising in fluctuations of the structure of the lipid double layer. Ion transport with participation of complex forming agents (ionophores) takes place to a limited extent under native conditions.

2. The conductivity of a single ionic channel has multilevel character owing to the possibility of the formation of metastable conformations of the protein subunits of the ionic channels.

3. The selectivity of the ionic channels is determined by the different capacity for hydration of the transported ions and by the presence of regulatory ("gate") polar fragments in the vicinity of the entrances to the channels.

4. The state of the surfaces of the biological membranes (surface enzymes, receptor sections) can determine to a large extent the selectivity of the transmembrane ion transport, the transfer of information within the cell by changing either the charge state or the chemical activity of the surface enzymes as a result of a change in external factors.

5. The transport of ions and water molecules across biological membranes can be achieved under highly non-equilibrium conditions.

6. The transport processes in membranes are highly non-stationary; individual stages of the transport are coupled with conformational transformations in membrane fragments.

7. The ion transport in membranes is influenced decisively by the local electric field within biological membranes. By means of a redistribution of the charge density and by the creation of additional and local electric fields (relative to those already existing), the "mild" utilisation of the energy evolved in the organism in a wide variety of energy dependent processes occurring *in vivo* is achieved, especially in the active ion transport in ATPase (Na^+, K^+-ATPase, Ca^{2+}-dependent ATPase, the H^+-ATPase of the internal membranes of mitochondria) and photodependent (BR) transport enzymes.

8. Ultrahigh temperature thermal fluctuations, occurring in biological systems which are thermodynamically open, have a decisive influence on the characteristics of the activated (including transport) processes in biological membranes and are responsible for the non-Arrhenius character of the activated process.[11,12]

The native systems are immeasurably more complex than the synthetic systems and one can therefore speak merely of a comparison of the most general principles of the functioning of transport systems *in vivo* and of the processes involving the separation of liquid and gaseous mixtures using synthetic membranes in intense mass and electromass transfer. Under intense conditions of membrane separation, the permeability of artificial membranes and the selectivity of the transport through them of different components (ions, molecules) actually depend greatly on the characteristic of the structure, in particular the submicrostructure, of the membrane, of the kind which obtains in biological membranes. The possibility of increasing the efficiency of membrane separation methods actually consists in the specific formation of the structure and state of the surfaces of the membranes in order to impart to them the required properties.

III. THE NATURE OF THE SELECTIVE TRANSPORT OF COMPONENTS IN SYNTHETIC MEMBRANES

The mechanisms of the transport of ions and molecules in synthetic membranes of different types are extremely varied, although they are evidently not as complex as in native membranes. In the analysis of the principal features of ion and molecule transport through synthetic membranes given below we shall concentrate attention on the elucidation of the causes of the selective transport of the components of liquid and gaseous mixtures in polymer membranes which are most widely and effectively employed in membrane technology.

1. Separation of Components in Baromembrane Processes

Reverse osmotic, ultrafiltration, and microfiltration processes are classified as baromembrane processes. The last two processes are evidently determined by the dimensions of the membrane pores or, more precisely, by the pore size distribution function (the characteristic ranges of pore sizes in ultrafiltration and microfiltration membranes are respectively $R_{uf} \simeq 5-50$ nm and $R_{mf} \simeq 0.1-10$ μm). The principal requirements which must be met by such membranes are high thermal and chemical stability (in the first place because of the necessity for periodic regeneration of the membranes by washing in special solutions) and relative uniformity of the pores as regards size when the porosity of the membrane is high.

The characteristic pore sizes in reverse osmosis membranes, $R_{os} \lesssim 1-5$ nm, make it possible to retain the hydrated ions present in solution and at the same time to let through, with a definite degree of selectivity, molecules of different nature (for example, in the separation of mixtures of water with alcohol). A decisive role can then be played not by sieve effects, as in ultrafiltration and microfiltration, but by the influence of the field of surface forces[13,14] (dispersion, Coulombic, and structural forces[15]) on the species (ions and molecules) passing through. The efficiency of the operation of reverse osmosis membranes is therefore determined not only by the pore size distribution but also by the chemical structure of the polymer—the type of functional groups and their mutual disposition in space.

In asymmetric, first-generation, reverse osmosis membranes based on cellulose acetates, the structure of the selective layer (its thickness is usually ~0.2 μm) was not sufficiently rigid. In the course of the functioning of such membranes, some rearrangement of the structure apparently takes place and submicrochannels, which pass through the selective layers and through which a stream of solvent molecules moves (for example, in the demineralisation of salt solutions),[16] are formed.

New generation reverse osmosis membranes permitting the large-scale desalination of natural waters (brackish water, sea water) have been created recently. Composite membranes obtained on microporous polysulphone supports by the interfacial polycondensation of aromatic diamines (for example, *m*-phenylenediamine) with tricarboxylic acid chlorides (for example, trimesic or cyclohexane-1,3,5-tricarboxylic chlorides[17,18]) have the most effective functional parameters. Such aromatic polyamide coatings are characterised by high chemical, mechanical, and thermal stabilities owing to the rigid three-dimensional structure of the polymer molecules resembling the structure of a non-ordered zeolite. High permeability to water (~ 1 m^3 m^{-2} day^{-1}) with a salt retention up to 99.5% at working pressures in the range 20–30 MPa, which are anomalously low for reverse osmosis (on membranes of previous generations such efficiency was achieved at pressures in the range 5.0–6.0 MPa), is then ensured. However, an inadequate stability in relation to sterilising agents, including chlorine, is characteristic of such membranes, which limits the scope of their use for water treatment and for the processing of industrial waste. Increased resistance to oxidants is attained for polymeric materials not containing NH groups, in particular, polypiperazinamides. The corresponding reverse osmosis membranes (developed by the Separam Company) with a selectivity with respect to NaCl of about 95% and an efficiency of ~ 1.0 m^3 m^{-2} day^{-1} (at a working pressure of ~4MPa) are stable in salt solutions at a chlorine concentration of 50 p.p.m.

When water flows during the desalination process through the rigid system of submicropores (cavities) and channels of the selective layer of reverse osmosis membranes, the salt retention is determined both by the size of the channel, connecting the hydrated cavities, and by the random force field generated by all the fragments of the polymer in the region of the channel.

For the calculation of the hydrodynamic resistance of the selective layer, one can use the approaches based on theories of the flow of liquid in a random labyrinth[19,20] which were developed earlier for problems concerning the transport of a non-wetting liquid (for example, mercury) in porous materials.[21,22] According to Neimark,[22] it is useful to represent the pore distribution in space in the form of a three-dimensional lattice whose linkages (edges) correspond to the pore channels and the nodes correspond to the sites of their intersection, i.e. the cavities. In this approach, the problem of the relative distribution of the liquid and gaseous phases (the cavities and channels which are respectively filled and unfilled by water molecules) reduces to the classical problem of the theory of flow—the problem of percolation via connections.[19]

We shall consider the process involving the "forcing" of a non-wetting liquid into a pore system.[22] At an excess pressure P, the non-wetting liquid can be forced through pore channels whose effective size exceeds a certain quantity R_+, which depends on P and the field of surface forces in the channel. Such pore channels with $R > R_+$ will be called supercritical. The fraction p of supercritical pore channels is determined by the channel size distribution function $\varphi(R)$:

$$p = \int_{R_+}^{R_{max}} \varphi(R)\, dR.$$

Considering the liquid phase in terms of the macroscopic approximation, it is convenient to introduce the concept of the surface tension (coefficient) σ_s at the liquid–vapour interface and of the wetting angle θ. For a cylindrical pore, $R = 2\sigma_s \cos\theta/P$.

At an excess pressure P, the non-wetting liquid penetrates only into the pores which are linked to the outer surface of the specimen by a sequence of supercritical pore channels. It is known that for $p < p_c$, where p_c is the lattice percolation threshold, the probability of the existence of a continous sequence of supercritical channels decreases exponentially with increase in the length of such sequence. Under these conditions, the non-wetting liquid penetrates only into supercritical pores in the immediate vicinity of the outer surface. Only when the excess pressure increases so much that the fraction p of the supercritical pore channels exceeds the percolation threshold p_c does the non-wetting liquid penetrate into the bulk of the specimen. The corresponding pressure is referred to as the break-through pressure. Its value p_c is determined from the relation

$$p_c = \int_{R_+(P_c)}^{R_{max}} \varphi(R)\, dR. \qquad (1)$$

The phenomenon of break-through (the penetration of a non-wetting liquid into the bulk of the specimen) at $p > p_c$ is due to the formation of an infinite connected system of supercritical pores or of an infinite cluster (IC). The IC incorporates cavities (nodes) and supercritical channels (edges or connections) and the cavities are connected to the outer surface by a continuous sequence of supercritical channels. For large specimens containing a macroscopically large number of elementary pores, one can neglect the edge effects and assume that the IC is distributed uniformly in the bulk of the specimen and that the degree of saturation (it characterises the relative volume of the liquid phase in the overall volume of the system of pores and channels) of a specimen having finite dimensions is equal to the corresponding quantity for a semi-infinite medium.

We shall assume that the pore channels of different sizes are distributed at random. Then the distribution of the supercritical channels in the lattice will also be random: the probability that an arbitrarily selected connection is supercritical is equal to the fraction p of the supercritical pore channels. The following characteristics of the IC are considered in the percolation theory: the connectivity function $Q_c(p)$—the fraction of connections included in the infinite cluster among all the lattice connections; the percolation probability $Q_p(p)$—the fraction of nodes included in the IC relative to all the lattice nodes; the relative conductivity $\sigma(p)$—the ratio of the lattice conductivity, in which conductors constitute a fraction p and the fraction of insulators is $1 - p$, to the conductivity of the lattice in which all the connections are conductors. The characteristics of the relative phase distribution are expressed in terms of these functions. In the example considered, the non-wetting liquid occupies the pores incorporated in the IC formed by supercritical connections and the degree of saturation λ is expressed in terms of the connectivity function and the percolation probability:

$$\lambda = v_p Q_p(p) + (1 - v_p) Q_c(p), \tag{2}$$

where v_p is the fraction of the volume of the cavities in the overall pore volume and $1 - v_p$ the fraction of the volume of the pore channels.

The effective transport coefficients of the liquid in the system of channels are porportional to the conductivity of the IC:

$$D(\lambda) = D(1)\sigma(p), \tag{3}$$

where $D(\lambda)$ and $D(1)$ are the effective transport coefficients for a degree of saturation λ and for the complete filling of the pore space respectively.

The connectivity function, the percolation probability, and the relative conductivity for a simple cubic lattice have a non-linear threshold character and are identically equal to zero for $p < p_c$. Such behaviour is typical for any lattices regardless of their topology. The percolation threshold is mainly determined by the lattice coordination number z. The approximate equality $p_c \simeq 1.5/z$ is known to hold. In the vicinity of the percolation threshold, the asymptotic scaling relations are valid:

$$Q_p \propto Q_c \propto (p - p_c)^{\beta}, \tag{4}$$

$$\sigma \propto (p - p_c)^{t}. \tag{5}$$

The critical indices of the percolation probability (β) and conductivity (t) are[22] in the ranges $0.35 < \beta < 0.47$ and $1.5 < t < 2.0$. Under conditions remote from the percolation threshold, the linear equation of the self-consistent field theory is valid for conductivity $\sigma(p)$:

$$\sigma(p) = \left(p - \frac{2}{z}\right)\left(1 - \frac{2}{z}\right)^{-1}. \tag{6}$$

The percolation probability $Q_p(p)$ and the connectivity function $Q_c(p)$ can be fitted[23] by a power relation; at $p \gtrsim 2p_c$, they differ little from the asymptotic relations:

$$Q_p(p) \to 1, \quad Q_c(p) \to p. \tag{7}$$

According to the scaling hypothesis, the geometry of the percolation system, including the structure of the IC, is determined by a single characteristic dimension—the correlation length L. Under conditions remote from the percolation threshold at $(p - p_c)/p_c \simeq 1$, the correlation length can be of the same order of magnitude as the size $\overline{R}_1$ of a single structural element. At $p \to p_c$, the correlation length increases without liimit in accordance with the power law

$$L \propto (p - p_c)^{-1+\delta}. \tag{8}$$

The critical index of the correlation length for three-dimensional lattices is $1 - \delta \simeq 0.9$.[22] For distances $r \gg L$, the IC is homogeneous and for $r \ll L$ a correlation in the distribution of elements belonging to the IC is manifested. In the vicinity of the percolation threshold, where $L \gg \overline{R}_1$, there is a region where $\overline{R}_1 \ll r \ll L$, in which the IC possesses the so called fractal properties, i.e. it is characterised by a non-traditional dependence of its volume (or surface) on the geometrical scale. For example, the number of elements in the IC at a distance $r' < r$ from a selected element increases in proportion to r^{d_f}, where the so-called fractal dimensionality d_f is not equal to the dimensionality of the space d:

$$d_f = d - \beta/(1 - \delta) \tag{9}$$

(in the three-dimensional case, $d_f = 2.5$). Ideas concerning fractal properties of the IC proved fruitful in the study of the geometrical features of the relative distribution of phases in the pore space.

The dependence of the relative conductivity σ on the fraction of the elements incorporated in the IC is of interest for the calculation of the effective transport coefficients in partly saturated porous media. It follows from the scaling relations (4) and (5) that

$$\sigma \propto Q_p^{t/\beta} \propto Q_c^{t/\beta}. \tag{10}$$

From Eqn.(2), it follows that in the scaling region the effective transport coefficients with respect to the non-wetting phase are linked by a power relation to the degree of saturation and that the power exponent is equal to the ratio of the critical indices of the relative conductivity and the percolation probability:

$$D(\lambda) \propto \lambda^{t/\beta}. \tag{11}$$

An interpolation expression for $D(\lambda)$ has also been obtained:[22]

$$D(\lambda) = D(1)\frac{2.88}{(1 + 1.31v_p)^{3.48}}\lambda^{3.48} \quad \text{for } \lambda < 0.433(1 + 1.31v_p). \tag{12}$$

The characteristic features of the penetration of a non-wetting liquid into porous systems can be analysed on the basis of Eqns.(11) and (12) as a function of the applied pressure. However, for the corresponding analysis of the permeability to water of reverse osmosis membranes it is essential to possess independent data on the structural parameters of the selective layer, including the pore size distribution function and the surface force field parameters. Unfortunately, there are virtually no such data at the present time. When the appropriate investigations are carried out, it will become possible to assess more effectively the potential possibilities of the method of reverse osmosis for the separation of various, including aqueous organic and organic, liquid mixtures. At the present time relations of type (11) and (12) have been established for gas and electrolyte transport processes in porous nickel electrodes.[24]

Ultrathin surface layers of submicroscopic thickness (~10 nm), made of organic and inorganic (for example, polyphosphazenes) materials and produced on ultrafiltration or microfiltration supports, can serve as carrier structures with fractal properties in the separation of mixtures of electrolytes, in the separation of gaseous mixturres under intense separation conditions, and in electrocatalytic processes. Not only the corresponding permeability constants but also the parameters of the selectivity of the separation can then depend on the thickness of the ultrathin layer. The ways of creating such structures can be related to the use of the Langmuir–Blodgett method for the formation of monomolecular films and mixed structures with a high degree of molecular order and of the electrochemical, plasmachemical, and photochemical methods for the deposition of ultrathin layers. In fact one is dealing with a qualitatively new level of membrane technology, because the permeability

of the membranes to the target components increases by more than an order of magnitude and hence there is a significant decrease in the materials consumption in the membrane process. The technical sophistication involved in the creation of such barrier structures and ultrathin layers must be the highest possible and must involve an ultrapure technology (as regards materials and the concentration of aerosols in the surrounding space) employing the experience and methods of electronic industry.

2. The Diffusion-Migration Transport of Species in Membranes

In many synthetic membranes, molecules and ions are transported via a mechanism involving the dissolution of the components in the membrane matrix and the subsequent diffusional or diffusional-drift transport through the bulk of the membrane. In membranes of this type (ion-exchange and gas separation membranes) there are no rigidly fixed pores, although they do possess a definite free volume. In the case of flexible chain polymers, the effects associated with the redistribution of the free volume due to the mobility of fragments of the matrix play a decisive role in transport processes.[25] In rigid chain polymers (below the glass point T_g), the efficiency of the transmembrane transport of species is usually correlated with the structural non-equilibrium nature of the polymer matrix, characterised by the presence of definite submicrocavities in the vicinity of bulky substituents in the side chains.[26–28]

The traditional method of describing mass and electromass transfer processes in non-porous membranes involves the use of quasi-equilibrium ideas and the neglect of the "surface resistance", it being supposed that the transport of ions and molecules through the boundary regions takes place at a high rate (at the membrane–medium interfaces, there is equilibrium with respect to the species which have crossed the membrane). Therefore, if the membrane separates two volumes of gas with different concentrations of species of one kind, then, together with the consideration of local values of the diffusional flux of species in the membrane

$$J = -D\frac{\partial c}{\partial x} \quad , \tag{13}$$

where $c(x, t)$ is the local concentration of species in the membrane, D the diffusion coefficient, x the coordinate normal to the surface of the membrane, and t the time, it is necessary to introduce the sorption isotherm of the component in order to determine the concentrations of species near the surface. On the simplest assumptions concerning the form of the isotherm (the Henry isotherm), an expression follows from Eqn.(13) for a stationary flux of species passing through the membrane:

$$J = \Pi\Delta P/d;\ \Pi = D\gamma \quad , \tag{14}$$

where Π is the permeability constant of the material, γ the thermodynamic parameter of the solubility of the component in the given material (the Henry constant), ΔP the drop of the pressure of the component across the membrane, and d the thickness of the membrane. If the species migrating in the bulk of the membrane is acted upon by lateral forces—in the presence of an electrical potential gradient $\partial\varphi/\partial x$ (transport of particles with an electrical charge q) and also in the presence of a convective flux (for example in the case of transport in liquid and quasi-liquid membranes)—then the expression for the local flux of species J assumes the form

$$J = -D\frac{\partial c}{\partial x} - c(x)\cdot\left[\mu\frac{\partial\varphi}{\partial x} - u\right] \quad , \tag{15}$$

where μ is the electrical mobility of the species linked to the coefficient D by the Einstein relation $\mu = \xi qD/k_BT$ (T is the absolute temperature, k_B the Boltzmann constant, and $\xi \simeq 1$ a phenomenological numerical parameter) and u is the rate of drift of the species under the influence of the convective movement of the medium. The use of Eqn.(15) together with the sorption isotherm of the component transported in the membrane makes it possible to generalise Eqn.(14) and to take into account simultaneously the diffusion, electrodiffusion, and convective diffusion processes.

In considering the diffusional transport processes in real solid-phase membranes, inorganic and polymeric organic, complications arise due to the presence in them of different kinds of inhomogeneities: structural defects and inclusions of another phase. These defects and inhomogeneities can serve as capture sites for the given species, can give rise to local mechanical stresses influencing the transport processes, can effectively sort the diffusing components, etc. The description of mass transfer in such inhomogeneous media is complex even under the conditions of small fluxes of the transported species. The situation becomes immeasurably more complex if it is necessary to take into account non-linear effects associated, for example, with the characteristics of the sorption of the diffusing components in an inhomogeneous matrix.[29] Intuitively it is clear that the description of the transport of species must be based on the use (appropriately justified) of effective diffusion coefficients D_{eff}, which depend on the characteristic features of the transport of the species in those regions of the membrane which are characterised by different equilibrium solubilities of individual components and also on the spatial distribution of such regions in the matrix.[30]

3. Non-Equilibrium Transport Conditions

The traditional quasi-equilibrium approach to the description of processes involving the membrane separation of the components of gaseous and liquid mixtures is justified only for a low density of the fluxes J_i of the components i crossing the membrane, when $J_i \ll J_{io}$, J_{io} being the "exchange flux" density of the component i in the regions of the membrane–external medium interfaces and also at the boundaries between the micro- and submicro-regions in the bulk of the membrane differing in structure. In such cases there is equilibrium with respect to the species i in different regions of the system and the fraction of the species passing to each of the structurally different regions within the membrane is determined by the thermodynamic parameters of these regions.

On passing to extremely highly non-equilibrium regimes in membrane separation under the conditions of electrodialysis, electrolysis, and elevated pressures in gas separation, when $J_i \lesssim J_{io}$, the quasi-equilibrium models of the "dissolution and diffusional-migration transport" become inadequate. Under these conditions, the state of the membrane–medium interface determines the character of the distribtuion of the transported species between the external medium and the membrane. The state of the boundary separating regions with different physicochemical characteristics in the bulk of the membrane determines the distribution of the pathways (fluxes) of the species in the membrane matrix and, with increase in J_i, the condition $J_i \simeq J_{io}$ begins to hold at a greater number of interfaces. It therefore becomes necessary to consider in previously structurally indistinguishable regions increasingly finer details (with dimensions down to several nm), which influence the redistribution of the species in the matrix under the conditions of intense mass transfer. The transport of molecules and ions through synthetic membranes

acquire certain features characteristic of the most effective membranes—namely biological membranes, both as regards the type of organisation of the transport (transport via "channels") and as regards the principal kinetic relations.

We shall consider below a series of problems in the model description of transport processes in membrane systems under extreme regimes and shall demonstrate what new possibilities can arise in the membrane separation of liquid and gaseous mixtures under these conditions.

The transition from quasi-equilibrium mass transfer regimes to extreme (non-equilibrium) regimes can be conveniently illustrated in relation to the transport of the molecules of simple gases through membranes based on siloxane–containing block copolymers. A relation between Π and ΔP has been observed[32,33] in a study of the permeability of such membranes to the molecules of simple gases (CO_2, O_2, and N_2), which consists in a considerable (severalfold) increase in Π when P changes from 1 to 5 kPa. According to quasi-equilibrium ideas, Π = const if D and γ are independent of pressure. In an analysis[34] of the sorption isotherms of the molecules of simple gases (CO_2 and O_2) in siloxane-containing Silar block copolymers, no anomalies were noted: the adsorption isotherms were linear throughout the experimental pressure range (up to 75 kPa). It is therefore most natural to assume that, under conditions[32,33] where $P > 5$ kPa, the filling of both phases of the block copolymer, rigid and flexible, is non-equilibrium and transport takes place mainly in the flexible phase. The latter conclusion is also confirmed by the results of a study[35] in which correlations were observed between the mobility of the fragments of the siloxane phase of the block copolymer and the effective diffusion coefficients.

On passing to non-equilibrium mass transfer regimes, the effective solubility parameter σ differs from the equilibrium value γ ($\sigma < \gamma$), which leads to the possibility, in principle, of influencing the permeability constants of membranes by modifying the membrane–medium interface. This possibility has been realised in a study[36] where it was shown that the chemical modification of the gas–polymer interface by the polymerisable fluorine-containing allyloxysilane, which exhibits surface-active properties, can increase almost by a factor of two the permeability constants Π of the modified membranes relative to the corresponding values for the initial (unmodified) membranes. Under the conditions of such modification, the diffusion coefficients D of gases in the membranes remain almost unchanged and DSC [differential scanning calorimetry?] data also indicate the unchanged state in the bulk of the membrane after its modification: the thermograms of the initial and modified membrane are completely identical. The equilibrium value γ should not therefore change as a result of the above modification and the observed effect must be attributed to a change in the effective solubility: $\sigma_{mod}/\sigma_{init} \simeq 2$.

In order to solve the problems of membrane separation in non-equilbrium transport regimes, another procedure is needed, in particular the use of the method of the theory of flow (of a liquid in a random labyrinth).[19–20] Here the effective pathways in the transmembrane transport of species ("infinite clusters"—IC, in terms of the terminology of the theory of flow) are produced by a system of localisation centres separated from one another by an optimum average distance. This situation obtains in the transport of ions through perfluorinated sulphonic acid cation-exchange membranes characterised by a specific submicrostructure characteristic of comb polymers: the hydrophobic matrix at the hydrated ionogenic group in the amorphous regions of the perfluorinated polymer forms associated species—"clusters" with characteristic dimensions of ~ 5 nm.

A fragment of the amorphous part of the perfluorinated sulphonic acid cation-exchange material is illustrated in Fig.3. According to this structural model, the pathways followed in the flow of ions and water molecules are within ion-exchange clusters ("ionic channels" in a hydrophobic matrix). The transport of ions over macroscopic distances (the formation of IC) becomes possible for a sufficiently high degree of hydration of the ionogenic groups (centres between which ion jumps are effected), whereupon an effective linkage is established between adjacent ionogenic groups.

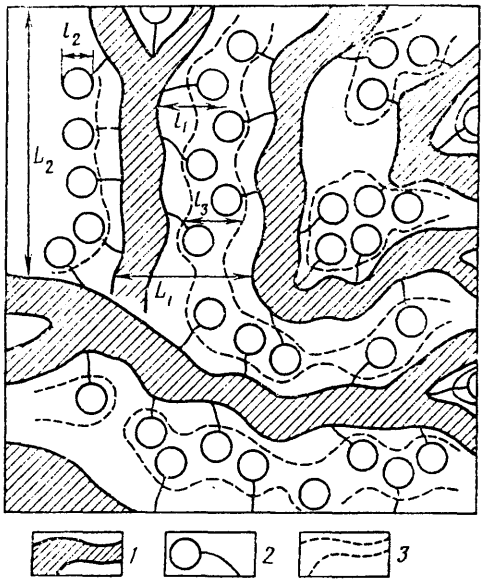


Figure 3. Schematic illustration of a fragment of the amorphous part of a sulphonic acid cation-exchange membrane:[37] 1) main polymer chain; 2) hydrated counterions and ionogenic groups under the conditions of a low moisture content (the "chlorine electrolysis" conditions); 3) "channels" for the transport of ions and water molecules in the presence of a high moisture content; the distance $L_1 \simeq$ 4 nm is estimated from low-angle X-ray scattering data, $L_2 \simeq$ 10 nm from Mössbauer spectroscopic data, l_1 and l_2 from DENR and NMR data, and l_3 from data obtained by reference porometry and DENR.

Under the conditions of a high moisture content when the average number of water molecules n per ionogenic group exceeds 15, virtually all the functional groups of the membrane are "bound" and the polymer matrix is on average uniformly threaded by a random network of channels hydrated to the maximum extent, through which the diffusional transport of ions takes place. The specificity of such ionic transport is low.

With decrease in the moisture content, some of the "bonds" between adjacent centres are broken so that "dead ends" appear in the random network of channels.[20] In the flow model, the dependence of the specific resistance of the membrane ρ on the moisture

content for low values of n ($n < 10$, "chlorine electrolysis" conditions) is of the form[37]

$$\rho \simeq \frac{R_0 r_c}{[\nu(n) - \nu_c]^{2-\delta}} \cdot \exp\left[p\,(\bar{n}^{1/s} - n^{1/s})^{\mu_s} + \frac{\varepsilon(n)}{k_B T}\right], \qquad (16)$$

$$p = \left[2\alpha_s \left(\frac{3}{4\pi\rho_0}\right)^{1/s}\right]^{\mu_s}, \quad \bar{n} = \frac{1}{6}\pi\rho_0 r_c^3,$$

where R_0, α_s, and μ_s are parameters determining the probability of the jump by ions between adjacent ionogenic groups, $\varepsilon(n)$ is the activation energy for such a jump, $\nu(n)$ the average number of bonds between a specified ionogenic group and adjacent groups whose centres are separated from the centre of the specified group by distances not exceeding the characteristic average value r_c, ν_c is the threshold value of $\nu(n_c)$ for which IC arise, and ρ_0 is the effective density (packing density) of water molecules in the hydrated ionogenic group–counterion complex.

Attention should be drawn to the decisive role of the entropy factor in Eqn.(16) which depends exponentially on n and is determined by the parameters α_s, μ_s, and r_c in establishing the specificity of the ionic transport. A similar situation apparently arises also in the ionic transport in biological membranes. In the region of low values of n, the following relations between the quantities ρ for ions of different types (for a fixed n) are valid in the case of sulphonic acid cation-exchange membranes:

$$\rho_{H^+} < \rho_{Li^+} < \rho_{Na^+} < \rho_{K^+} < \rho_{Cs^+}.$$

Analysis of the relation obtained permits the conclusion that there is contact interaction of the hydrated cation with the ionogenic centre (the sulpho-group), which is consistent with Eisenman's series XI in the binding of ions within the channels of membranes capable of being excited.[38] This means that the ionic channels of sulphonic acid cation-exchange membranes are systems with a high "field strength" (such as, for example, the Na^+-channels in the squid axon). The creation of membranes with other types of ionogenic groups ensures new possibilities for the selective transport of ions and leads to the realisation of other Eisenman selectivity series (for example, among the eleven which exist for cations).

Spectroscopic studies using ^1H and ^7Li NMR[19] have shown that the character of the relation defined by Eqn.(16) is determined by the characteristics of the elementary ion transport between the functional groups. This means that the specificity of ion jumps under the conditions of limited capacity for hydration of the functional groups (this situation actually obtains also in the ionic channels of biological membranes) is associated with the entropic multipliers of the rate constants for the corresponding jumps. For ions of different types, one may point to certain critical values of n_i such that, for $n < n_i$, the transport of ions of type i is significantly retarded as a consequence of the formation of cation–functional group contact ion pairs. When sulphonic acid cation-exchange membranes are used, these values for the H^+, Li^+, and Na^+ ions are respectively ~ 2, ~ 4, and ~ 6. In particular, this is indicated by the dependence of the chemical shift of the water protons in the membrane on the moisture content of the latter:[39] for $n > n_i$, the ions indicated retain their individuality in the membrane—they exist in the form of the complexes $[H_5O_2]^+$, $Li^+.4H_2O$, and $Na^+.6H_2O$.

One of the main consequences of Eqn.(16) is large local heat evolution in perfluorinated membranes when a high-density electric current j passes through them (under the conditions of "chlorine electrolysis" and $j \simeq 0.3$ A cm^{-2} and when the overall moisture content in the membranes is low, we have $\nu \gtrsim \nu_c$ because of the high concentration of the resulting alkali, reaching 20–40%). It has been shown [20] that, in the vicinity of the flow threshold, the bulk of the Joule heat is evolved within a small volume on a limited number of "bonds" (at the "heating points")[40] and in the limit $\nu \to \nu_c$ the fraction of the volume carrying almost the entire Joule heat tends to zero.

Before discussing certain consequences arising from the above, we may note that perfluorinated ion-exchange membranes are "non-cross-linked". Therefore, under the influence of local heat evolutions, the conformation of the polymer chains in the membranes may change, giving rise to the formation of metastable structurally-conformational states of the amorphous fragments with an arrangement of the side chains characteristic of each such state.

For sufficiently extreme electromass-transfer regimes under the conditions of a low moisture content in the region of the "heating point", there is a possibility of a virtually complete dehydration of the functional groups, so that the probability of ion jumps in this region falls sharply and the corresponding transport section is eliminated from the IC. However, the "evaporated" water molecules formed on dehydration can hydrate functional groups which had not been previously included in the IC and a new percolation pathway arises. The above mechanism of the "flickering of transport pathways" ensures high thermal stability of the non-cross-linked perfluorinated ion-exchange materials.[37]

One may note that the effective mechanical properties of the non-cross-linked copolymers, necessary for the functioning of the membrane in such extreme regimes, are determined by the PTFE crystallites ensuring the "physical" reinforcement of the perfluorinated matrix. Such crystallites (their characteristic size is ~ 10 nm) are formed by fragments of different copolymer molecules without functional groups. The intermolecular distances realised in PTFE crystallites at room temperature are attained in PTFE crystals at elevated temperatures (470–490 K). Closer packing of the above fragments is prevented by the presence of functional groups in the macromolecules. In order to diminish the "wedging" influence of the ionogenic groups on the PTFE crystallites, perfluorinated membranes are obtained from ternary copolymers [in particular, in polymerisation one introduces, apart from tetrafluoroethylene and the perfluorinated ester with sulphonyl fluoride or carbonyl fluoride groups, a third monomer of the type $CF_2 = CFO(CF_2)_3CF_2$, which is responsible for the formation of buffer zones between the PTFE crystallites and the amorphous section containing ionogenic groups; this improves the mechanical properties of the membranes].

4. Characteristics of the Transport of Species in Liquid and Quasi-liquid Membranes

A promising development is the use of liquid and quasi-liquid† membranes for the selective extraction of target components. It has been suggested that they be used[41,42] especially for the extraction of metals in hydrometallurgical industries, for the concentration of valuable components in waste and natural waters (including sea water). In this connection, a series of problems arise: (1) the development of a scientific basis for the search for complex-forming

†Quasi-liquid membranes or impregnated liquid membranes are understood to constitute liquid systems (the solvent with the complex-forming agent, catalyst, etc. contained in it) immobilised in an inert porous base; in the foreign literature the term "supported liquid membranes" is usually employed for such membranes.

agents ensuring a high extraction selectivity; (2) stabilisation of complex emulsions ("Li membranes"[43]) and film systems (in Boyadzhiev's columns) for the solution of technological problems in liquid membrane extraction; (3) enhancement of mass exchange processes in the region of the liquid membrane–liquid medium interfaces.

We shall confine ourselves to considering only mass exchange processes without dwelling on problems of the description of transport in the region of membrane–medium interfaces in view of the necessity to use boundary conditions of a fairly general type.[16]

As shown previously by Lev and Buzhinskii,[45] the formation of complexes in the interfacial region by the transported species with complex-forming agents present in the liquid membrane may retard the process and lead to the appearance of "surface" resistance. However, the situation can become still more complex when such complex formation occurs in macroscopic (~ 1 μm) regions of liquid membranes, for example, as a consequence of the formation in such layers of submicrodispersions of the external (in relation to the membrane) solution. In this field, there are still many fundamental difficulties to be overcome.

We shall consider the problems of mass transfer associated with its enhancement by spontaneous convection, which may develop in the boundary regions of the liquid membrane (and the electrolyte if it constitutes a medium external in relation to the membrane).[46] We shall confine ourselves to considering the classical problem of the transport of CO_2 molecules through liquid and quasi-liquid membranes formed on the basis of aquous alkali metal carbonate solutions, in connection with the results obtained recently,[47] which demonstrated the fundamental role of the effects of the spontaneous convection of the solution in this process.

The mechanism of the transport of CO_2 through liquid alkali metal carbonate layers can be represented in a simplified way by the following two stages:[48]

(1) dissolution of carbon dioxide accompanied by a heat change of ~ 26.2 kJ mol^{-1}:

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- ;$$

(2) the transport of HCO_3^- ions through the membrane and the evolution of carbon dioxide on the other side of the membrane where the CO_2 partial pressure is reduced and the reverse reaction

$$2HCO_3^- \rightarrow H_2O + CO_3^{2-} + CO_2$$

takes place. The process is accelerated when catalysts are introduced into the system, such catalysts frequently consisting of the anions of weak acids, for example, arsenic acid.

The kinetics of the transport of CO_2 through a liquid membrane consisting of a layer of liquid (3.2 *N* Cs_2CO_3 + 0.25 N Na_3AsO_3 solution; pH 13.6) enclosed between two hydrophobic asymmetric polyvinyltrimethylsilane films have been investigated.[47] These films exhibit a high gas permeability (the permeability to CO_2 is 3×10^{-8} mol m^{-1} s^{-1} Pa^{-1}), so that they do not introduce any distortions into the measurements (error $\leqslant 0.5\%$). The kinetics of the transport of carbon dioxide were investigated for the horizontal and vertical positions of the cell. For the horizontal position of the membrane, CO_2 was supplied to the cell in two ways: in one case carbon dioxide was injected into the upper cavity and a carrier gas (helium) into the lower cavity, while in the second case the opposite arrangement was used. As a result, the coefficients of the gas permeability Π of membranes of different thickness d were found at +20 °C.

It was noted[47] that, for the horizontal position of the cell, a steady increase in Π with increasing d was observed. The permeability coefficients depended on the way in which gas was supplied into the cell, the difference between the values of Π increasing with decrease in the thickness of the membrane. For the vertical position of the cell, Π initially increased with increase in d and then fell sharply. The values of Π for different orientations of the membrane differ by more than an order of magnitude (for $d = 3600$ μm).[47] Such behaviour of Π can be explained only by convective movements in the solution.

The appearance of convective movements within the liquid membrane can be caused by different factors. In particular, the heat evolution of dissolution of CO_2 induces local heating in the membrane and hence changes in the surface tension at the gas–liquid interface leading to Marangoni effects. It is therefore of interest to calculate formally the diffusion coefficient D and the solubility σ_{eff} of CO_2 molecules in the carbonate solutions on the basis of the model of the transmembrane gas transport, which includes the instantaneous dissolution and diffusional transport as the limiting stage. According to this model, $\Pi = D\sigma_{eff}$. The results of such calculation, based on the solution of the diffusion equations with boundary conditions of the first kind, have shown[47] that the values of D and σ_{ef} vary non-monotonically as the thickness of the membrane is altered. Starting with $d = 2600$ μm, the diffusion coefficient increases sharply while the solubility coefficient diminishes. Such behaviour of D and σ_{eff} may be caused by the initial stages in the development of the convective movement indicated. By reducing diffusional restrictions, these movements diminish the solubility coefficients. The induced transport of CO_2 molecules through the membrane takes place with participation of the "carriers" of these molecules—HCO_3^- ions. The low rate constant for the dehydration reaction $HCO_3^- \rightarrow CO_2 + OH^-$ (10^{-4} s^{-1} [49] at pH > 8) can mean that the process has two rate-limiting stages—transport and chemical stages, whose characteristic times are comparable. Therefore the lifetime of these carriers may prove to be of the same order of magnitude as their residence time in the region of the liquid–gas interface, which ultimately diminishes σ_{eff}.

The liquid and also quasi-liquid membrane described are characterised by a unique selective permeability to CO_2. Thus the ratio α of the permeability constants of such membranes for CO_2 and O_2 is $\sim 10^2 - 10^3$. Despite the fairly large number of studies devoted to gas transport processes through quasi-liquid membranes, the question of the contribution of the individual stages of these processes (diffusion, solubility) to the establishment of the high selective permeability of the membrane to CO_2 nevertheless remains obscure. Furthermore, the influence of the inert base on the kinetic characteristics of quasi-liquid membranes and on the methods of stabilisation of these characteristics has not been elucidated.

An attempt to find an answer to these questions has been made in a study[47] of inert, alkali-resistant polymeric matrices into which solutions of 3.2 *N* Cs_2CO_3 and a catalyst (0.25 *N* Na_3AsO_3) had been introduced. The choice of these particular substances (whose concentrations correspond to the saturation of the solution by caesium bicarbonate when CO_2 is passed through) is determined by the high gas permeability coefficients of such membranes. Hydrophilic porous filters based on UEM-270 ethylcellulose with an average pore diameter $I = 27$ nm and a thickness $d = 72$ μm, and also the polysulphone UPM ($R = 50$ nm, $d = 100$ μm) and poly(vinyl chloride) ($R = 170$ nm, $d = 100$μm) have been used as polymeric matrices.

The relative pore volume was estimated from the difference between the weights in the moist and dry states and was found to be 73% for UEM-270, 58% for UPM, and 76% for PVC.

The corresponding $\sigma_{eff}(P)$ relations were calculated from the experimental[47] permeability coefficients Π and the effective diffusion coefficients D of carbon dioxide in quasi-liquid membranes and a number of conclusions were reached.

1. The carbon dioxide sorption isotherms (the dependence of the amount of CO_2 absorbed by the carbonate solution on its partial pressure in the gaseous mixture) is significantly non-linear and is almost independent of the nature of the polymeric matrix of the membrane.

2. The diffusion coefficient D increases with increase in the CO concentration in solution and depends greatly on the average pore size in the initial matrix. For relatively small average pore dimensions (27 and 50 nm), D is almost constant. However, the increase of R from 50 to 170 nm alters D almost by a factor of 5. Such behaviour of the diffusion coefficients can be explained by the appearance in the large pores of a kind of convective displacements of the structural units of the solution (associated ions and water molecules) as a consequence of the local heating of the solution during the course of the binding of CO_2 molecules.

3. The character of the variation of the permeability coefficient Π as the carbon dioxide pressure in the initial mixture is varied is associated with the antiparallel dependences of D and σ on P.

In conclusion of the Section, we shall discuss factors determining the high selectivity of the quasi-liquid membrane. The permeability, diffusion, and solubility coefficients of carbon dioxide and oxygen in the UEM-270 porous filters saturated with distilled water or the 3.2 N Cs_2CO_3 + 0.25 N Na_3AsO_3 solution are presented below (for $P_{CO_2} = P_{O_2} = 100$ kPa[47]):

		$10^{13}\Pi$, mol s^{-1} m^{-1} Pa^{-1}	$10^{10}D$, m^2 s^{-1}	$10^{4}\sigma$, mol m^{-3} Pa^{-1}
CO_2	H_2O	1.48	4.05	3.65
CO_2	3.2N Cs_2CO_3+0.25N Na_3AsO_3	2.74	$2.4\cdot10^{-2}$	$1.14\cdot10^{3}$
O_2	H_2O	$5.51\cdot10^{-3}$	4.0	$1.38\cdot10^{-1}$
O_2	3.2N Cs_2CO_3+0.25N Na_3AsO_3	$1.7\cdot10^{-3}$	$2.7\cdot10^{-1}$	$6.3\cdot10^{-3}$

For a membrane containing distilled water, $\alpha \simeq 27$. The selectivity of a quasi-liquid membrane increases to 160.

The example considered makes it possible to understand how high selectivity coefficients of liquid and quasi-liquid membranes can be attained and what are the possible ways of increasing the permeability to the target components. Here it is naturally necessary to achieve the stability of such systems, which may become a complex problem in their practical employment (for example owing to ageing or the elution of the reagents from the quasi-liquid membrane, as a consequence of the poisoning of the complex-forming carrier, owing to difficulties in its regeneration, etc.).

Microporous polypropylene,[50] polytetrafluoroethylene, poly(vinyl chloride), and polysulphone,[51] used in ultrafiltration and microfiltration processes, serve nowadays as bases for quasi-liquid membranes. Impregnation of such filters with liquid reactive carriers makes it possible to obtain membranes for the effective separation of liquids and gaseous mixtures combining the high efficiency of the porous membranes with the high selectivity of the carrier.[52–54] We may point to advances in the creation of highly selective membranes for the isolation of oxygen from air (the ratio of the corresponding permeability constants is $\sim 26-50$) which permitted the attainment of a nitrogen content in oxygen of only 9–15% after a single-stage separation.[55]

Liquid membranes of the emulsion type, stabilised by surfactants, have already found application in industry. In particular, the effectiveness of the use of such systems for the isolation of zinc[56] and sodium[57] ions, enzymes,[58] copper,[59] phenol,[60] and other organic and inorganic substances has been demonstrated (see also Van et al.[61]).

5. Membrane Processes Involving the Isolation of Vapour Mixture Components

New possibilities of the isolation of vapour components from liquids and vapour–gas mixtures have usually been attributed to the development of a new membrane process – membrane distillation.[62,63] We shall consider initially the simplest model ideas about the character of the movement of the gaseous mixture in porous systems in relation to transport in a straight cylindrical capillary.[64]

The movement of gases in such a capillary is determined by the Knudsen parameter Kn – the ratio of the number of collisions of the molecules with the walls to the number of intermolecular collisions. To within a constant multiplier of the order of magnitude of unity, the parameter Kn is equal to the ratio of the average length of the free path of the molecule l to the capillary diameter:

$$\mathrm{Kn} \simeq l/2r_c \qquad (17)$$

Since the lengths of the free path l_i of molecules in different gases in a gaseous mixture are of the same order of magnitude, the parameter Kn for a mixture of gases is approximately constant. Depending on the value of Kn, three characteristic gas flow regions are distinguished: the Knudsen region (Kn $\gg$ 1), the transitional region (Kn $\simeq$ 1), and the molecular region (Kn $\ll$ 1).

For Kn $\gg$ 1, the components of the gaseous mixture move through the capillary almost independently of one another. The total molar flux of the ith component under the conditions of Knudsen flow is therefore proportional to the gradient dc_i/dx of the molar concentration c_i of the component (the x axis is directed along the capillary axis):

$$J_i = c_i v_i = -D_i^K \frac{dc_i}{dx} = -D_i^K \left[c \frac{dy_i}{dx} + y_i \frac{dc}{dx} \right], \quad y_i = c_i/c, \; c = \sum_i c_i \qquad (18)$$

where D_i^K is the Knudsen diffusion coefficiient, c the total molar concentration, and v_i the velocity of the ith species along the capillary. For a cylindrical capillary under the conditions of diffuse reflection of the species from the walls (accommodation coefficient $\gamma_{a,i} = 1$), we have

$$D_i^K = \frac{2}{3} r_c \bar{w}_i \qquad (19)$$

where $\bar{w}_i = (8k_BT/\Pi m_i)^{1/2}$ is the average thermal velocity of type i molecules. If there are N such cylindrical pores per unit surface of the membrane, then the permeability constant Π_i of this membrane for type i molecules can be represented in the following form taking into account Eqn.(19) and the equation of state of an ideal gas:

$$\Pi_i = \frac{8R^3N}{3N_A} \left(\frac{\pi}{2m_i k_B T} \right)^{1/2} \qquad (20)$$

where N_A is the Avogadro number.

The relationship (Kn $\ll$ 1) obtains in fairly broad capillaries. The average linear velocities of the components are then constant along the section of the capillary, while the molar fluxes are related to the gradient of the driving forces by the Stefan–Maxwell system of equations. For constant P and T and also in the absence of external

forces, the Stefan–Maxwell system of equations can be conveniently put in the form

$$\frac{\mathrm{d}c_i}{\mathrm{d}x}=\sum_{i\neq j}(c_iJ_j^{T,P}-c_jJ_i^{T,P})/D_{ij}c \quad . \tag{21}$$

Here $J_i^{T,P}$ is the molar flux of the ith component for constant P and T and D_{ij} is the mutual diffusion coefficient of components i and j. Here we may note one non-trivial factor. Under the conditions of isobaric-isothermal molecular flow (Kn $\ll$ 1) of a mixture of gases in a long capillary, the interaction of the gas with the walls also proves very significant, since it determines the inter-relation between the partial fluxes. In order to obtain the corresponding conditions, we shall take into account the fact that, for a zero pressure drop across the capillary, the overall momentum $M_{\parallel}$, transmitted to the walls of the capillary when all the molecules of the mixture interact with them is zero:

$$M_{\parallel}=\sum_i M_{\parallel,i}=0 \quad , \tag{22}$$

$$M_{\parallel,i}=\frac{1}{4}c_i\bar{w}_im_iv_i(r_c)\gamma_{a,i} \quad .$$

Taking into account the relation $w_i \propto m_i^{-1/2}$, we find from Eqn.(22) the expression

$$\sum_i m_i^{1/2}\gamma_{a,i}J_i^{T,P}=0,$$

which yields the required relation for the case of the diffuse reflection of the component or for the independence of the coefficient $\gamma_{a,i}$ of the type of species:

$$\sum_i m_i^{1/2}J_i^{T,P}=0 \tag{23}$$

This is the so called Graham condition.[65]

In the case of a binary gaseous mixture with P = const. and T = const., we obtain from Eqns.(21) and (23)

$$J_i^{T,P}=D_{ij}(1-\alpha_{ij}c_i/c)^{-1}\frac{\mathrm{d}c_i}{\mathrm{d}x}=-D_{ij}c(1-\alpha_{ij}y_i)\frac{\mathrm{d}y_i}{\mathrm{d}x} \quad , \tag{24}$$

where $\alpha_{ij}=1-(m_j/m_i)^{1/2}$. Eqn.(24) has the form of Fick's law only for a small mole fraction ($y_i \ll 1$) of the diffusing component (diffusion of an impurity) or for the diffusion of components with the same molecular weights ($m_1 = m_2$); in the latter case $J^{P,T} = J_1^{P,T} + J_2^{P,T} = 0$.

The transitional regime (Kn $\simeq$ 1) in the flow of a gaseous mixture in capillaries is significantly more difficult to investigate. In the corresponding analysis, one usually employs interpolation formulae. The expression for the partial flux in the case of isobaric-isothermal flow of the binary mixture is usually represented in the form

$$J_i^{T,P}=-D_{b,ij}c\frac{\mathrm{d}y_i}{\mathrm{d}x} \tag{25}$$

and the Bosanquet expression [64] is used for $D_{b,ij}$—the binary diffusion coefficient in the transitional regime:

$$D_{b,ij}^{-1}=\frac{1}{D_i^K}+\frac{1-\alpha_{ij}y_i}{D_{ij}} \tag{26}$$

When transport in a porous medium is considered, the coefficients D_i^K and D_{ij} are usually renormalised by introducing into them the multiplier ε/ζ, where ε is the velocity of the material and ζ the tortuosity of the pores.

The above expressions for the fluxes of the components of gaseous mixtures in capillaries in different flow regimes can be used for the analysis of the problems of the membrane separation of gaseous and vapour–gas mixtures. In the first place, we have in mind here the Knudsen flow regime in which the mixture of gases passing through a porous membrane is enriched, in accordance with Eqn.(20), in the lighter components. However, such processes are not sufficiently effective owing to the relatively small mixture separation factors in cases of greatest practical interest. Admittedly, in the membranes with a continuous diffusion layer employed for technological purposes, the possibility of the existence of "through" submicrodefects and transport via such defects must be taken into account in accordance with the formulae quoted above.

The calculation of gas fluxes in capillaries is of greater current interest in connection with the development of the physicochemical principles of membrane distillation. This process consists in the selective mass transfer of water vapour through a finely porous hydrophobic membrane separating two aqueous solutions whose temperatures are different. The vapour molecules are transferred from the heated surface of the aqueous solution through the membrane pores and are concentrated on the cooled side. Evidently, the above process can find practical application (purification of sewage, desalination, concentration of solutions) in those cases where the cost of setting up a temperature gradient on the membrane is low (for example, when waste heat from industrial manufacturing processes is used). In the desalination of an NaCl solution, the flux $J = 3 \times 10^{-2}$ m^3 m^{-2} day^{-1} when the temperature difference between the two sides of a porous polypropylene membrane $\Delta T = 10$ K.[63] One of the advantages of the above process over distillation is the possibility of carrying it out for small temperature differences.

At the present time the membrane distillation method is used successfully not only for the purification of aqueous solutions with involatile solutes (salts, glucose) but also for the separation[69] and concentration[70] of mixtures (water–alcohol mixtures, for example) when all the components are volatile. Under these conditions, together with the traditional versions of the method, new ones are investigated:[69,71,72] membrane distillation with evaporation into a vacuum and membrane distillation with an air gap or "thermal evaporation" through a membrane (a distillate from a 3.4% aqueous NaCl solution has been obtained by this method[71]). In the application of the latest versions, the efficiency of the process increases significantly as a result of the possibility of maintaining a larger temperature difference.

Evidently, the methods indicated make it possible to achieve effective evaporation through porous membranes in contrast to the traditional processes involving evaporation through non-porous polymeric membranes.[35,36,73] However, the traditional method has not lost its importance, especially in connection with the development of the new membrane materials,[74] which retain their separating characteristics in the course of prolonged use. In evaporation through a non-porous membrane, the driving force of the process is the difference between the chemical potentials of the substance on the two sides of the membrane. The permeating substance is removed in the vapour phase by creating a vacuum or together with a stream of inert gas.

Like the membrane gas separation process, this process ensures a high degree of separation in a single stage at a relatively high flow rate through the membrane. It can be used for the separation of mixtures of hydrocarbons and aqueous organic mixtures and also for the dehydration of solutions. The possibility of separating with its aid azeotropic mixtures and mixtures with similar boiling points and solubilities is of greatest value. Since the efficiency of the separation in evaporation through a membrane is determined by the permeability constants, i.e. the products of the diffusion coefficients of the components and their thermodynamic solubilities, it follows that, in order to increase the selectivity of the transport, it is desirable to

introduce into the polymer matrix functional groups capable of interacting strongly with individual components of the mixture to be separated (for example, the introduction of electron-donating groups in the presence of electron-accepting molecules in the mixture[75]). This makes it possible to attain a high process selectivity (including the possibility of separating isomers[75]) by varying the chemical composition and structure of the polymeric selective layer in the composite membranes usually employed for such purposes (together with asymmetric polysulphone membranes). The idea of imprinting[76] (preliminary "tuning") of the polymer matrix with respect to species of a specific type, which increases the degree of selective sorption of the given component, is especially promising in this instance (as in reverse osmosis and gas separation processes).

We may also point to studies of the removal of traces of organic substances (chloroform, trichloroethylene, etc.) from water[77] and of the separation of water–alcohol[78,79] and other aqueous organic mixtures.[80,81] Composite membranes with a selective layer based on polyamidoimides and polyamides are effective for the separation of mixtures of water with acetic acid.[82]

In conclusion of this Section, we shall deal with the interesting phenomenon of the oscillation of the permeability and selectivity with respect to components migrating through a membrane, which has been observed in the evaporation of an aqueous solution containing 10 vol.% of isopropyl alcohol through an asymmetric polyvinyltrimethylsilane (PVTMS) membrane with a thickness of the active diffusion layer of 0.2 μm.[83] The experimental apparatus consisted of a thermostatted cell with a membrane fixed with a vacuum tight joint. On the side of the diffusion layer, the membrane was in contact with the liquid and on the opposite side there was a chamber, evacuated to a residual pressure of 0.1–1.0 Pa, containing a trap cooled with liquid nitrogen. In order to avoid concentration polarisation, the liquid was thoroughly stirred. The flux density was calculated from the mass of the condensed vapour which had passed through the membrane and its composition characterised the selectivity of the membrane. The amount of evaporated liquid constituted only a very small fraction of the initial amount, so that its concentration remained almost constant throughout the experiment. The auto-oscillatory regime was established after an induction period. Alcohol and water evaporated preferentially for the minimum and maximum flux density through the membrane respectively.

According to Ageev and Sekacheva,[83] the mechanism of the observed process is as follows. According to the conditions governing the formation of asymmetric membranes, internal stresses arise in the active PVTMS layer. When the polymer comes into contact with the solution of the alcohol, whose molecules in this case play the role of a surfactant, the strength of the membrane diminishes and the stretching forces due to the internal stresses become capable of causing local disruption of the material with formation of microcracks directed into the interior of the membrane. The surfactant migrates preferentially from the solution into the zone of the microcrack, since it is sorbed by the hydrophobic polymer significantly more effectively than water; this promotes the growth of the microcrack to a micropore characteristic of the porous layer of an asymmetric membrane. The stretching and compressing internal stresses diminish under these conditions. The walls of the micropore formed are "lined" with the surfactant, whose molecules are linked to the non-polar polymer via their hydrophobic component, while the hydrophilic component is oriented towards the body of the pore. The imparting of hydrophilic properties to the surface of the micropore promotes preferential transport of water molecules and an increase in the overall flux as a consequence of the decrease in the activation energy for the transmembrane transport. The increased water concentration in the pores induces the desorption of the surfactant, an increase in surface tension, and hence an increase in cohesive forces. The latter tend to decrease the surface area and the structure becomes continuous again. The collapse of micropores increases the stretching snd hence the compressing internal stresses. The mechanism of mass transfer changes to an activated one, which leads to the preferential migration of the surfactant and the process is repeated. Thus the oscillations in the flux and concentration are accompanied by oscillations in the internal stresses. As the internal stresses relax, the oscillations should decay. The oscillation period is related to the time of structural transitions which is controlled by the kinetics of the sorption and desorption of the surfactant.

The mechanism described can be regarded as the manifestation of the Rebinder effect in polymeric systems. Reversible structural transitions play in this instance the role of a kind of feedback relay issuing commands to include and exclude non-activated flow stages, which in fact leads to the oscillatory regime in the operation of the membrane. The corresponding mathematical procedures, adequately representing the phenomenon described, have been developed.[84]

IV. MEMBRANE CATALYSIS

New possibilities in the application of membrane technology are associated with the development of membrane catalysis – the creation of chemical reactors in which catalytic reactions on the surface or in the bulk of the membrane are combined with the simultaneous controllable supply of the initial reactant (frequently in a specified "activated" form) through the membrane to the reaction zone or the removal of the products from the reaction zone (situation characteristic of native system "bioreactors"). The possibilities of the selective transfer of the reactants or products through the membrane are naturally related to the difference between the permeability constants $\Pi_i = D_i\sigma_i$ for individual components.

Membrane catalysis was first applied in the hydrogenation reactions of hydrocarbons and the reaction of carbon monoxide with hydrogen using membrane catalysts made of palladium and its alloys.[85] The efficiency of such processes is determined by the high permeability of palladium membranes to hydrogen and the formation on their surface of catalytically active adsorbed atomic hydrogen.[86] Not only the catalytic activity of the catalyst but also the flux of hydrogen atoms arising from the bulk of the membrane to the surface (the atoms can carry a small effective charge[87]) depends on the state of the catalyst surface.

The use of membrane catalysts based on palladium and its alloys and also silver and nickel makes it possible to carry out various processes of practical importance with a high degree of efficiency: hydrogenation of acetylene to ethylene, of diene hydrocarbons to olefinic hydrocarbons, and of naphthalene to tetralin, dehydrogenation of alkenes and alkanes, etc. (see the articles contained in the compendium edited by Gryaznov and Klabunovskii[85]).

Membrane catalysts based on transition metal and rare metal oxides exhibiting a higher ionic conductivity at elevated temperatures have begun to be developed in recent years.[85–94] A wide-scale search is being prosecuted at the present time for systems of this kind, used in the first place for the oxidation of organic compounds. Processes involving the oxidation of ethylene[89] and propene[90] to the corresponding epoxides with separation of oxygen and the initial

hydrocarbon on the membrane, which was based on yttrium-stabilised zirconium oxides deposited on a porous silver catalyst, have been carried out. The O^{2-} ions are electrochemically "pumped up" through the solid electrolyte to the catalyst. The selectivity of this process is appreciably higher than in the case where molecular oxygen is supplied to the system (without "pumping" O^{2-}). When scandium- or yttrium-stabilised zirconium oxides were used as the solid electrolyte (membrane), it was possible to achieve also the oxidative dehydrogenation of ethylbenzene.[91] The removal of oxygen from platinum and gold catalysts significantly increased the rate of decomposition of NO.[92] Analogous studies have been carried out on the oxidation of SO_2,[93] the electrochemical oxidation of H_2, CO, and CH_4,[94] etc.

In a number of studies bismuth oxide stabilised by the addition of other oxides was used as the solid electrolyte. Such systems are stable up to 800 °C and exhibit a high conductivity with respect to oxygen ions.[88] In particular, the $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ system has been used not only as a membrane separating atmospheric oxygen from the given reagent (propene in helium) but also as the catalyst of the oxidative dehydrodimerisation of propene.[88] Dissociative adsorption and reduction of molecular oxygen take place on the catalyst surface on the air side; the oxygen ions then migrate to the opposite side of the catalyst membrane where they substitute the ions of the lattice oxygen functioning as the oxidant. The selectivity in the formation of C_3 dimers was greater than in the case where oxygen and propene were supplied from one side; there is no loss of catalytic activity if the rate of the process is limited by the supply of oxygen ions to the reaction surface.

There is no doubt about the likely usefulness of such research, because an increase in the process selectivity frequently plays a decisive role in the assessment of the economic value of a particular method of synthesis of the required product. Further progress will also be associated with the determination of the nature of the catalytic effect in the reactions investigated, the establishment of the role of promoting additives, and the search for methods for additional activation of the catalyst surface.

The nature of the catalytic activiy of solid-phase systems is associated primarily with the specific features of the submicrostructure in the catalyst regions near the surface (characteristic size $\sim$1–10 nm) and with the distortion of the equilibrium configuration of the ligands and hence with the decrease in the symmetry of the local environment of the "active centre", which may be a transition metal ion or group of ions. The symmetry of the crystal field acting on such a centre is then reduced compared with the symmetry typical for an equilibium matrix. As a consequence of this, the parameter Δ of the splitting of the d levels of the transition metal ion in the active centre diminishes, which leads to a rearrangement of the electron sybsystem of the centre and an increase in the fraction of the high-spin state of the ion with an increased catalytic activity.[95]

Apart from structural factors, the chemical activity of the surface layers of the solid-phase matrix can depend significantly on its dynamic properties. In the region of structurally non-equilibrium fragments, the vibrational relaxation time of the local thermal excitations,[96] whose energy exceeds the strain energy of the structurally non-equilibrium matrix, can be significantly retarded. For this reason, catalytic reactions in the course of which thermal energy is locally evolved and there is a possibility of a rearrangement of the matrix, can exert an additional influence on the activated processes occurring in the matrix, including their influence on the kinetics of the catalytic processes proper, and can lead to a non-Arrhenius character of the temperature variation of the rate constants.[11,12,96]

We may also note the role of the conformational mobility of the structural fragments in the region of the active centre, which is responsible for the increase in the entropic factor governing the rate constant for the elementary reaction and increases the probability of the realisation of the "lock and key" relationship in the substrate–active centre system.[97]

All the factors indicated can influence the kinetics of the catalytic reaction on the surface of an inorganic membrane and further experimental studies promoting the elucidation of the role of each of them are therefore essential (the application of Mössbauer spectroscopy for this purpose is extremely effective[95,97]).

One may note yet another factor which is important in the analysis of the catalytic process with participation of oxygen – the presence of different, in the simplest case two, forms of adsorbed oxygen: the weakly chemisorbed (non-reconstructive) form, exhibiting as a rule an increased reactivity,[98,99] and the "deep (reconstructive) form of adsorption" involving stronger binding to the surface.[99] These forms obtain in the adsorption of oxygen both on oxide and metallic catalysts.[100–102] It has been suggested that the formation of these forms is due to adsorption on different active centres of the surface. One cannot rule out also another possibility – the formation of metastable adsorbed forms in adsorption on a single centre (for further details, see Savchenko[99]).

The quantum-chemical nature of the dual character of the adsorption of certain molecules on the same centres can be understood if account is taken, following Balabanov et al.,[103] of the exponential decrease in the intensity of exchange adsorbent–adsorbate interaction (the resonance integral) with increase in the distance of the adsorbate molecule from the catalyst surface. Here the energy of the ground state of the system is characterised by two minima located at different distances from the geometrical surface of the adsorbent and to which correspond bonds with different amounts of ionic character (a more covalent bond corresponds to a minimum at a greater relative distance). The above states of the molecule in adsorption can correspond to these minima: "closely bound" molecules and molecules adsorbed on the "outer surface" of the adsorbent (the weakly chemisorbed form). One of these states should be regarded as metastable. The appearance of a particular form of adsorption depends not only on the thermodynamic characteristics of the system but also on the adsorption conditions.

The formation of two forms of oxygen chemisorbed on metals has been considered.[101,104] As an example, we shall consider the possible reorganisation of the initial electronic structure of the real surface of silicon (an adequate set of experimental data exist for the system) in its electrochemical formation (as a consequence of the adsorption of the oxygen of water[105]). The SiO^- bond formed at the SiO_2–electrolyte interface is shorter (its length is 1.55 Å) than the Si–O–Si bridge bonds, because the extra electron pair at the anionic oxygen atom promotes the overlap of the p_π orbits of oxygen and the unoccupied d_π orbit of silicon, i.e. an increase in the $Si-O^-$ bond order (which is close to two).[106] If the initial dipole moment of the surface is such that the negative pole is directed to the outside (of Mikhailovskii et al.[101]), then such "contact" dipoles (the "strong form of chemisorption") can lead to a decrease in the initial dipolar jump in the vicinity of the $Si-O^-$ dipoles, i.e. the deformation of "holes" in the initial dipolar layer; the electrostatic field of the $Si-O^-$ dipoles can suppress[107] the anodic process, namely it can release positively charged ions into the electrolyte from the surface layers of SiO_2. The possibility of "controlling" the kinetics of chemical reactions on the SiO_2 surface thereby arises, provided that they are associated with the transport of positively charged ions through the

SiO_2–electrolyte interface. Evidently, when the SiO_2 surface is formed in another way (in the absence of anodic polarisation), the $Si–O^-$ dipoles are not formed and a weak chemisorption form of the silicon–oxygen bond, activating the anodic process, arises.

Such opposite (or sharply different) influences of various forms of adsorption of molecules on the kinetics of interphase physicochemical processes occurring with their participation can apparently be regarded as a fairly general phenomenon. In particular, on the basis of the model proposed, ideas can be developed[108] concerning the dependence of the atomic catalytic activity on the amount of ionic character of the metal–oxygen bond and ways of increasing the catalytic activity of the catalysts, including membrane catalysts, can be sought by means of a specific treatment of their surfaces. Here one must bear in mind that additional heating with subsequent quenching can accelerate the activated transitions of molecules between different adsorption states[98] and, in particular, can activate the reactive forms.

Membranes obtained by immobilising fragments of biological systems (enzymes or whole bacterial cells) on inorganic and organic supports or on polymers of different nature have the most unique catalytic properties. The high efficiency of such systems is manifested in organic synthesis[109] and in biotechnology (the preparation of aliphatic acids and glycerol from vegetable oils,[110] the conversion of lactose into glucose and galactose,[110] the manufacture of caffeine,[111] antibiotics,[112] etc.).

Further progress in this direction will undoubtedly be associated with the discovery of methods for the stabilisation of the funcional characteristics of such membrane reactors and with the search for methods of intensifying the processes including the procedure involving a change in the conditions of such processes and in the external influences. The creation of jumps in the electrochemical potentials of different ions on either side of the basic synthetic membrane (of the type of the liposomal membrane), on which enzymes are immobilised, may prove effective. The opposed or unidirectional ionic fluxes ("antiport" or "symport") through the basic membrane arising in this instance alter the local composition of the electrolyte in the vicinity of the immobilised enzymes and thereby influence the rate of formation and the yield of the reaction products. The use of photodependent systems, in particular of bacteriorhodopsin in order to couple processes involving the utilisation of light energy and the enzymic reaction proper, appears promising.[113]

V. CONCLUSION

Evidently the advances in the construction and creation of membrane reactors for the solution of biotechnological problems will be determined by the advances in the study of not only the general principles but also of the details of the functioning of the native systems.

The investigation of ion and molecule transport processes in synthetic membranes can in its turn contribute new ideas to the understanding of the characteristics of the functioning of the native systems. As mentioned above, ionic transport in the channels of perfluorinated sulphonic acid cation-exchange membranes under the conditions of limited ion hydration can model the transport in the channels of biological membranes – the elementary jumps of the ions between adjacent functional groups. Studies on the transport processes in vitreous polymers make it possible to put forward hypotheses concerning the nature of the multilevel character of the conductivity of the native ionic channels. The study of the characteristics of ionic transport in synthetic membranes and of the effects of concentration polarisation in the regions of the electrolytes adjoining the membranes has created a basis for a number of hypotheses[1] about hitherto puzzling effects of the action of electromagnetic radiation on biological systems.[114]

In the analysis of the most complex and artificially nonreproducible biological phenomena, one must bear in mind the idea expressed by Frenkel':[115] "the more complex the system considered, the simpler should be, through necessity, its theoretical description ... a good theory of complex systems should constitute merely a good "caricature" of the systems, exaggerating their most typical properties and deliberately ignoring all other, insignificant properties". However, even in the creation of such "caricatures" a wide variety of models appear, which indicates the impossibility at the present time of identifying any unique fundamental schemes for the realisation of native processes. The clear inadequacy of the experimental data, especially under conditions *in situ*, must then be partly made good by intuitive ideas based on the knowledge of the physical chemistry of a wide variety of non-biological processes (catalytic, electrochemical, and mechanochemical). In the solution of the problems of the construction of bioreactors, the situation is somewhat simplified: there is no need to consider new concepts (apart from the known physicochemical ideas), because one is dealing with the characteristics of the functioning of only the individual units of complex biological systems and the most general problems of living organisms as essentially self-organising and self-developing systems are not involved.

The physical chemistry of the elementary processes in native and synthetic membranes is the same despite the immeasurably greater complexity of biological systems. Future advances in the sciences concerned with the study of transport processes *in vivo* and in artificial membranes, namely the understanding of the principles of the functioning of living systems and new practical achievements in mem-brane technology, can be seen to be engendered by the close inter-relation between such sciences.

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Modern Ideas About Diffusion in Polymer Systems

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The experimental data and theoretical approaches concerning processes involving the diffusion of low-molecular-weight substances in polymer systems are examined. Information is presented about the influence on diffusion of the degree of crystallinity and filling, of the physical state of the diffusion media and the size of spherulites, of the composition and structure of the copolymer macromolecular chains, and of the size of the diffusing molecules. The possibility of using diffusion measurements to investigate the phase and supermolecular structures of polymers, the construction of phase diagrams, and to determine the thermodynamic parameters of the interaction of the components of polymer solutions is demonstrated. The bibliography includes 101 references.

CONTENTS

I. Introduction 504
II. The influence of the nature of low-molecular-weight substances on their diffusion in polymers 505
III. The influence of the nature of the high-molecular-weight component 507
IV. Diffusion in heterogeneous systems 511
V. Diffusion methods for the study of polymer systems 515

I. INTRODUCTION

Considerable interest has been shown in recent years in the study of diffusion phenomena in polymers. In our country alone, a whole series of monographs[1-10] devoted to the consideration of various aspects of this problem were published between 1980 and 1987. There are several causes of such interest. Firstly, the vigorous development of membrane technology, the need to create effective anticorrosion polymer coatings, and the description of the kinetics of phase decompositions, structure formation, as well as polymerisation at high conversions require detailed information about the mutual diffusion and self-diffusion coefficients and their dependence on concentration, temperature, pressure, and phase and supermolecular structures of polymeric media. Secondly, the development of theoretical concepts, mainly reptation ideas concerning the translational mobility of macromolecules in solutions and melts,[10,11] has stimulated experimental studies on the molecular dynamics of chains[1,10] and the development of new methods for the investigation of the local mobility of end groups, monomeric units, and macromolecules as a whole.[8,9] The development of the theory of free volume and activation zones[7,10] plays an analogous role in the study of the diffusion of low-molecular-weight substances. Thirdly, the creation of effective methods for the investigation of mutual diffusion and self-diffusion, on the one hand, and the development of phenomenological and thermodynamic approaches,[12] on the other, promoted in their turn not only the solution of a whole series of practical problems but also the development of a new trend—the use of diffusion measurements for the study of molecular, phase, thermodynamic, and defect characteristics of polymer materials.[3,6,7,10,13]

Evidently, in a single review it is impossible to consider even in a concise form the present state of research into various aspects of the problem of diffusion phenomena in polymers. We shall therefore confine ourselves to a small group of questions which are fundamentally important both for the prediction of the separating properties of membranes and for the analysis of the characteristics of their formation and the determination of their structural-morphological and phase inhomogeneities.

The review does not discuss the question of the mechanism of the diffusion of low-molecular substances in polymeric media. However, one should bear in mind that, in considering research results, we were guided by the following postulates. The translational thermal movement of small molecules in polymers takes place, regardless of their physical state, as a result of consecutive elementary jumps over distances of the order of the molecular diameter of the diffusing species. The occurrence of an elementary jump requires the presence near the molecule of a microcavity—vacancy, whose volume v^* is greater than the volume of the diffusing molecule V or is comparable to it. A vacancy is formed via a thermofluctuation mechanism as a result of a set of small-scale segmental movements manifested in a β-relaxation process.[1,8,14] The rotation of low-molecular-weight species in polymer media is a faster process than translation and during the period of its "settled life" the molecule has sufficient time to undergo repeated changes in its orientation.[1]

Within the framework of a qualitative picture of the mechanism of diffusion in polymers, two virtually equivalent expressions are used for the diffusion coefficient:

$$D = D_0 \cdot \exp(-E/RT) \quad (1)$$

(the so called activated diffusion model) and

$$D = A_1 \cdot \exp\left(-\gamma \frac{v^*}{v}\right) \text{ or } D = A_2 \cdot \exp\left(-\frac{B}{f}\right) \quad (2)$$

(the free volume model). Here D_0, A_1, and A_2 are the pre-exponential factors, E is the apparent activation energy for diffusion, R is the gas constant, γ and B are constants, and v and f are the free volume and the fraction of the free volume in the diffusion medium. Different expressions for D_0, E, and f can be found in a number of publications.[1,7,10]

II. THE INFLUENCE OF THE NATURE OF LOW-MOLECULAR-WEIGHT SUBSTANCES ON THEIR DIFFUSION IN POLYMERS

It has been shown[1-10] that the rate of mutual diffusion and self-diffusion in polymer systems is determined not only by external factors (temperature, composition, and pressure) but by a whole series of internal parameters, which depend both on the individual characteristics of the system components and on the properties of the system as a whole. We shall enumerate some of them: molecular weight (M_1) and molecular weight distribution (MWD) of the polymer, the monomeric coefficient of friction, the microviscosity, and the thermodynamic non-ideality of the solution. The influence of molecular-chemical parameters of the low-molecular-weight component (diffusant, penetrant, sorbate, and solvent) and, in particular, its M_1 and the dimensions, shape, and structure of its molecules on its diffusion in polymeric media is considered in this Section. We may note that the determination of a quantitative relationship between the molecular characteristics of the diffusant and its diffusion parameters in polymers is one of the main problems of diffusion kinetics, because it opens up extensive possibilities for predicting the selective and protective properties of membranes, coatings, and shells.

1. The Influence of the Molecular Weight of the Diffusant

In considering the influence of the molecular weight of the molecules diffusing in polymers on D, one usually employs the empirical Auerbach equation

$$D = KM_1^{-b} , \qquad (3)$$

where K nd b are constants. This type of relation is common to all cases of translational migration of molecules in viscous media and, from a formal point of view, it follows from hydrodynamic ideas concerning diffusion.[15] Eqn.(3) holds both in low-molecular-weight media, for example in the diffusion of saturated hydrocarbons, alcohols, diols, and triols in benzene, methanol, and water,[2,16] and in the diffusion of macromolecules in infinitely dilute solutions; in the former case, $b = 1$, while in the latter b varies from 1/2 to 1.[15,17]

The diffusion of low-molecular-weight substances in polymeric media of different nature is in most cases described satisfactorily by Eqn.(3). Comparative analysis of the numerical values of the constants of Eqn.(3) for different homologous series, carried out by a number of investigators,[2,7,9] permits the following conclusions. Firstly, Eqn.(3) holds as a rule within the limits of a single homologous series of diffusants, for example, $Y-(CH_2)_n-CH_3$, i.e. when the functional group P is constant and only the number of repeating units n changes. When Y is altered, i.e. on passing from one homologous series to another, the $\lg D - \lg M_1$ plot shifts along the ordinate axis, but b remains almost unchanged. This effect is observed, for example, for polybutadiene, polyethylene, polyisoprene, and polyvinyltrimethylsilane on passing from saturated hydrocarbons to their isomers, alkylbenzenes, and dibasic saturated and aromatic acid esters.[7,9]

Secondly, for polymeric media, we have $b > 0.5$ and its value increases on passing from one polymer to another in proportion to the increase in their molar cohesion energy δ_2 (δ_2 is the solubility parameter[18,19]). The quantity K varies in inverse proportion to the monomeric coefficient of friction of the macromolecules ξ and the molar volume of the diffusing molecule or functional group V_x. The following expressions have been proposed:[7]

$$b = 1.4(\delta_2 - \delta_0) \text{ and } K = kT/V_x\xi,$$

where k is an empirical constant and δ_0 the minimum value of δ_2 for polymers.[18] This makes is possible to estimate the diffusional component of the separation coefficient for the polymer membrane:

$$\alpha = \frac{D_i}{D_j} = \frac{V_{xj}}{V_{xi}}\left(\frac{M_i}{M_j}\right)^{-1.4(\delta_i-\delta_0)} , \qquad (4)$$

where the indices i and j denote diffusants of different nature.

Thirdly, cyclic, halogen-containing, and aromatic compounds with condensed benzene rings constitute a special group among hydrocarbons. For these classes of diffusants, as for azo-dyes and antioxidants,[20,22] the slope of the $\lg D - \lg M_1$ straight line is fairly large ($b \geqslant 4$). Two factors should be noted: (1) the $\lg D - \lg M_1$ straight lines for the above systems intersect on extrapolation with the corresponding straight line for saturated hydrocarbons at the point which corresponds to the molecular weight of methane; (2) when a new repeating group, for example CH_2, is introduced into the molecules of these compounds, they initiate new $\lg D - \lg M_1$ straight lines. The unusual behaviour of diffusants of these classes compared with open-chain hydrocarbons is due to the fact that the introduction of a certain repeating group alters not only M_1 each time but also the cross-section of the diffusing species.

Finally, the displacement of the functional group along the skeleton of the diffusant molecule and the change in its nature for V_x = const. as a rule do not affect D even if one is dealing with the translational diffusion of polar substances in polar polymers.[23,24]

Together with the molecular weight, in the analysis of diffusion processes involving low-molecular-weight substances in polymeric media the geometrical parameters of the diffusing molecules are widely used: the molar volume V, the length l, and the cross-section σ. The above data permit the claim, in our view, that the molecular weight as well as other indirect characteristics (the critical volume V_{cr}, the constant b_W in the van der Waals' equation, and the viscosities of liquids) play the role of independent arguments in the equation for the rate of transport only because they characterise the geometry and structure of the diffusing molecules. For example, the relation between D and M_1 for the homologous series of alkanes is determined by the fact that M_1 is directly related to the length of the molecules; in the case of cyclic hydrocarbons, the variation of M_1 characterises to a first approximation the variation of the cross-section of the diffusing molecules. The role of the geometrical constants of molecules diffusing in polymeric media has been examined in a number of studies.[24-30]

The free volume model is the most convenient for the analysis of the influence of molecular volume on the diffusion of molecules in polymers. It is natural to suppose that the critical volume of the vacancies is proportional to the molar volume of the diffusing molecule: $v^* \cong aV$, where a is a constant. Evidently a similar relation can be formulated also for V_{cr} and b_W. On substituting these relations in Eqn.(2), we obtain the expression[7]

$$\ln D = \ln A - \gamma \frac{a}{v} V \qquad (5)$$

The activated diffusion model, where it is assumed that $E = E_0 + bV$, leads to an analogous result.[6,10,31]

Analysis of the experimental data within the framework of this approach showed[3,7,9,20,31] that, for the majority of systems where the shape of the diffusant molecules is close to spherical, a satisfactory agreement with theoretical predictions is observed. The experimental points corresponding to different representatives of homologous,

genetic, and, what is especially important, isolytic series are disposed in the vicinity of $\ln D - V$ straight lines whose slope is determined by the average free volume of the polymeric diffusion medium.

However, in the case of significantly asymmetric diffusant molecules, even for members of a single homologous series, Eqn.(5) is valid only to a first approximation. This is associated with the fact that, in the derivation of Eqn.(5), no account was taken of the specific features of the structure of both the diffusant molecules and the vacancies in the polymeric medium: they were all represented approximately by effective spheres, in conformity with the solid sphere model. On the other hand, it has been noted[7] that a is a function of the ratio σ/l; the smaller a is, the smaller is the ratio σ/l. Analysis of these data permitted[7] a number of conclusions concerning the character of the orientation of molecules in polymeric media relative to the direction of the diffusion flux. It was established that the transverse dimensions of the vacancies for linear and bulky molecules are significantly smaller than their length and effective cross-section (solid sphere) and are identical—for members of the given homologous series—with the dimensions of the largest functional group. For all the members of a single homologous series, the cross-sections of the vacancies remain unchanged. Under these conditions, they depend only slightly on the nature of the polymeric medium in which the diffusion process takes place.

From this it follows that molecules with a complex structure are oriented in the diffusion flux relative to the concentration gradient in such a way that they suffer the least resistance from the polymer matrix.

2. Activation Energy for Diffusion and Molecular Size

Depending on the structure and shape of the diffusant molecules, they can be divided into four groups: spherical, non-spherical, bulky, and linear.

Spherical molecules. This group includes, for example, the inert gas molecules. Analysis of experimental data has shown that the number of studies of diffusion in the same polymers of four and more types of spherical molecules is small.[31,32] For these diffusants, E increases with increase in the diameter d of the molecules (Fig.1). On passing from one polymer to another, the character of the dependence of E and d remains the same and only its steepness changes. Thus the dependence of E and d for polydimethylsiloxane can be fitted by the power equation $E \propto d^n$, where $n = 1$; for *cis*-polyisoprene and polyethylene $n = 2$ and for poly(vinyl acetate), poly(vinyl chloride), and poly(ethyl methacrylate) $n = 3$. Thus the power exponent increases with increase in the molar energy of cohesion of the polymeric medium. The unusual behaviour of E for diffusion in polar and non-polar polymers at temperatures above the glass point is striking. For the diffusion of He and Me in polyisoprene and polyethylene, E was found to be greater than for the diffusion in poly(vinyl acetate) and poly(ethyl methacrylate), while the opposite effect was observed for Ar, Kr, and Xe.

The experimental relations between E and d for the simplest diffusants cannot be fully accounted for within the framework of the Meers, Brandt, Pola–Di Binedetto, and Pace–Datyner models,[10,33,34] although they all correctly predict the qualitative picture of the changes in the activation energy for diffusion as a function of the molecular diameter, the size of the macromolecular segment, and the molar energy of cohesion of the polymeric medium. It has been shown[7,35] that a balanced approach requires not only the introduction of two different expressions for the energy formation of vacancies in the diffusion medium ($E_g \propto X^2$ and $E_g \propto X^3$, where X is the diameter of the vacancies) but also the allowance for the character of the distribution of vacancies with respect to size. Only then is it possible to explain also the anomalies in the variation of E for $d \leqslant 2.8$ Å and the dependence of E on the previous thermal history of polymer membranes.[36]

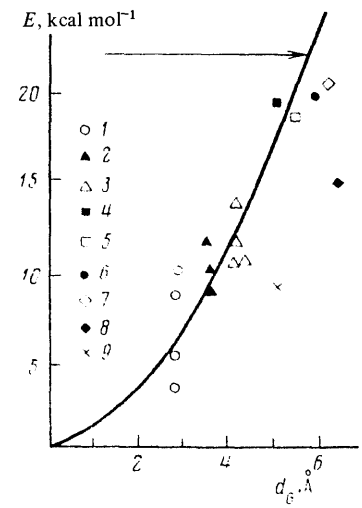


Figure 1. Dependence of the activation energy for the diffusion of gases in polyethylene on their gas-kinetic diameter:[7] 1) He; 2) Ne; 3) Ar; 4) Kr; 5) Rn; 6) CCl_4; 7) $C(CH_3)_4$; 8) SF_6; 9) CH_4. The continuous curve was calculated by the equation $E \propto d^n$, where $n = 2$; the arrow denotes the activation energy for the viscous flow of the polyethylene melt.

Non-spherical molecules. The molecules of simple gases can be included in this classes of diffusants: H_2, N_2, O_2, CO, CO_2 etc. By analogy with the inert gases, the gas-kinetic diameter d_G is usually employed as the main parameter characterising their dimensions. However, the behaviour of these molecules in diffusion processes in gaseous and condensed media is fundamentally different. Non-spherical molecules in the gas phase exist most of the time in a state of "free motion" and they interact with one another during a relatively short fraction of the time. During their movement, the molecules rotate freely, which leads to the absence of a correlation and the mutual orientation of the molecules during subsequent collisions.

In a polymeric phase the position is different. The dissolved gas molecule vibrates most of the time in a cell[1] until a vacancy of specific size appears next to it. For a spherical molecule, it is immaterial on which side a vacancy appears provided only that the relation $X > d$ holds. The situation is different for non-spherical molecules. Their shape can be represented approximately by an ellipsoid of rotation[37] with longitudinal ($d_{\|}$) and transverse ($d_{\perp}$) dimensions. Evidently, since $d_{\|} > d_{\perp}$, the probability of the appearance of

a vacancy with $X \geqslant d_{\perp}$ is greater than that of the appearance of a vacancy with $X \geqslant d_{||}$. Therefore the gas-kinetic diameters of these molecules are always greater than the diameters of the vacancies.[35,37]

The following mechanism has been proposed[32,37] for the determination of the effective sizes of non-spherical molecules diffusing in polymers. It is based on the experimental graphical dependence of E on d for the diffusion of inert gases in the given polymer. The effective diameter d_{eff} of any molecule, including a non-spherical molecule, can be determined from this relation and the activation energy for the diffusion of the diffusant investigated, which is also found experimentally. It has been shown[7] that d_{eff} for diffusing molecules changes somewhat (up to 8%) both on passing from one polymer to another and when the conditions in the preparation of the same polymer are altered. Thus, for this group of diffusants one can use in the calculation of E the power relations $E \propto d^n$, which have been obtained for spherical test molecules, but for d one must use not the gas-kinetic but an effective molecular diameter.

Bulky molecules. The CH_4, CCl_4, $C(CH_3)_4$, C_6Cl_6, SF_6, etc. molecules belong to this class of diffusants. If their size is estimated from d_6 or from the structural diameter, than the values of E for such substances should not fit on the relation between E and d obtained for the inert gases (Fig.1). The values of d_{eff} found by the above method for these molecules are always smaller than d_G and for bulky molecules the discrepancies are greater than in the case of non-spherical molecules. Graphical analysis[37] has shown that the minimum dimensions of the molecules which determine their motion in the polymer matrix are similar for all the substances enumerated.

A characteristic feature of bulky molecules is their variable diameter along the threefold symmetry axis in the tetrahedron [CH_4, CCl_4, $C(CH_3)_4$] and along the fourfold axis in the octahedron (SF_6). Thus in methane the apical atom has a diameter of 2.34 Å, while the diameter of the plane of the base of the pyramid is 4.4 Å. For sulphur hexafluoride, these values are 1.86 and 6.4 Å. Comparison of these quantities shows that the diameters of the apical atoms are always smaller than the values of d_G, which are in their turn smaller than the molecular sizes in other cross-sections. It follows from the foregoing that vacancies whose critical diameters are smaller than d_G are responsible for the migration of bulky molecules in polymeric media.

Linear and chain molecules. For diffusants of this class, the parameter characterising the molecular size used traditionally has been either their molecular weight, or the number of repeating groups, or the number of carbon atoms in the chains n_C. For these systems, the dependence of E on M_1 can be fitted by the semi-empirical expression

$$E = A + B \lg M_1 , \qquad (6)$$

where A and B are empirical constants. The method described above has been used[7,37] to estimate the sizes of vacancies through which the elementary step in the translational movement of oligomeric and polymeric molecules takes place. Comparison of the relations between E and n_C for different members of the homologous series of olefins, including polyethylene melts,[2,10] with the corresponding relation between E and d for the molecules of ideal gases shows that the size of the vacancy changes from 3.4 to 5.6 Å on passing from methane to a polyethylene macromolecule with $M \cong 10^5$. Assuming that the movement of linear molecules takes place via the reptation mechanism, it is easy to demonstrate that 4–5 monomeric units participate in the formation of the reptation loop of the polyolefin.

Theoretical studies on the activated model of diffusion in polymers have been directed mainly towards the development of the ideas of Brandt and Meers. At the present time the most effective molecular theory of diffusion is the Pace–Datyner theory,[33,34] which made it possible to obtain analytical expressions for D_0 and E in the Arrhenius equation on the basis of information about the macromolecular structure, crystallographic data, intermolecular interaction parameters, and the molecular diameter. One should also note a theoretical study[35,37] in which an attempt was made to take into account the contribution to E by the size distribution of the free volume vacancies of the polymeric medium. In these investigations, expressions were obtained for the average size of the free volume vacancy and the average size of the vacancy participating in the elementary diffusion step; the form of the relation between E and d was discovered and a formula was proposed for the determination of the volume of activation. Presumably these investigations permit the solution also of the converse problem—the determination of the size distribution of the free volume vacancies in the polymer membrane from data for the diffusion of the inert gases.

III. THE INFLUENCE OF THE NATURE OF THE HIGH-MOLECULAR-WEIGHT COMPONENT

1. The Influence of the Molecular Weight, the Molecular Weight Distribution, and the Three-dimensional Cross-linking

The influence of the molecular weight (MW) of the polymers on their permeability to gases and vapour has been most fully studied.[20] It has been found that a change in the MW of the macromolecules in the diffusion medium from 1×10^4 to 1×10^6 does not affect the rate of transport of gases and vapours. A small change in the permeability of polyisobutylene to moisture (from 10.7×10^{-13} to 3.3×10^{-13} mol cm^{-2} cm^{-1} h^{-1}) has been noted after an increase in its MW from 4.5×10^3 to 25×10^3.[38] The influence of the MW of polymers on the diffusion of monomers, solvents, and oligomers has been studied in less detail.

Most of the experimental data obtained for such systems refer to infinitely dilute solutions of polymers.[10,15] For this range of concentrations in binary systems, the mutual diffusion coefficient D_{21}, characterising the translational mobility of macromolecules in solvents, varies with the MW of the polymer (M_2) in accordance with the equation

$$D_{21} = K M_2^{-b} , \qquad (7)$$

where K and b are constants. Individual investigations have been carried out in the field of concentrated solutions.[2,7] With increase in the MW of the polymer, the diffusion coefficients in these solutions either remain unchanged, as, for example, in the benzene–polycarbonate, benzene–polystyrene, and octadecane–*cis*-polyisoprene systems or decrease, tending asymptotically to their limiting values for a certain M_2', as has been observed, for example, in the dioctyl phthalate–poly(vinyl chloride) ($M_2' = 4 \times 10^4$), cyclohexanone–polyhydroxyesters ($M_2' = 1.5 \times 10^4$), and hexadecane–polyethylene ($M_2' = 5 \times 10^3$) systems. The polystyrene–cyclohexanol, polybutadiene–diheptyl phthalate, and polyhydroxyesters–dibutyl

phthalate systems, for which the mutual diffusion coefficient in the middle range of solution compositions increases with increase in the MW of the polymer, are exceptions.

In the middle 1970s, the interest in this problem grew again in connection with the creation of telomers and oligomers with a narrow MWD and the development of methods permitting the measurement of the partial mobilities of solution components.[10,11] Interesting results were obtained for the influence of the MW of the polymeric component on the self-diffusion (D_1^*) and mutual diffusion (D_V) of the solvents and empirical relations linking D_V and D_1^* to the MW of the polymers were proposed;

$$\lg D_V = \lg D_{V,\infty} + A/M_2 \text{ and } \lg D_1^* = \lg D_{1,\infty}^* + B/M_2 , \quad (8)$$

where A and B are empirical constants and $D_{i,\infty}$ are the diffusion coefficients at $M_2 \to \infty$. It was shown that the anomalies described above in the variation of the diffusion coefficients are associated with the thermodynamic non-ideality of the systems and the remoteness of their state from the critical state.[2-10]

It has been shown[2,7] that the problem of the influence of the MW of the macromolecules on the diffusion properties of polymer matrices and membranes can be approached from the standpoints of the free volume theory, because the fraction of the free volume of the diffusion medium f depends on M_2 as a consequence of the variation in the number of end groups per unit volume. It follows from the statistical theory of polymers and the results of numerical modelling that the Brownian movement of the end groups of linear macromolecules is more intense than the thermal movement of the units of the main chain. This effect has been called the "hot ends" effect.[11,39] Semiquantitative estimates have shown that the end groups of macromolecules possess kinetic energy which is greater by 20–25% than that of the internal groups.[40] Frenkel' suggested that the mobility of the end groups be characterised by the diffusion coefficient of the monomer.[41] Direct estimates of the rotational and translational mobilities of the chain units and end groups of macromolecules in the condensed phase and in solution have been made.[1,42]

All these factors make it possible to attribute to the end groups of the macromolecules a local free volume different from the local free volume of the main chain units and the monomer. The average free volume of the diffusion medium made up of such molecules can then be represented by the sum of the local free volumes. In accordance with this hypothesis, the following relations have been obtained for polymer melts:

$$\ln \frac{D}{D_\infty} = \frac{B}{f_\infty} \cdot \frac{aM_2^{-1}}{f_\infty + aM_2^{-1}} , \quad (9)$$

$$\lg D \simeq \lg D_\infty + A/M_2 . \quad (10)$$

The last equation holds for $M_2 > 10^3$. Here a and A are constants and f_∞ is the fraction of the free volume of the polymer membrane at $M_2 \to \infty$. It can be seen that Eqn.(10) agrees fully with the empirical expressions (8). These equations have been used in calculations from experimental data of the numerical values of the free volumes corresponding to the end groups (f_e) and the monomeric units (f_{un}). It has been shown that $f_{un} < f_e < f_1$, where f_1 is the free volume per unit of monomer. Under these conditions, f_e is greater by 15–30% than f_{un}. The quantity f_e can be regulated by varying the chemical nature of the functional end group.[43]

In conclusion of this Section we may note that, firstly, the diffusion coefficients of low-molecular-weight substances in polymer glasses also decrease with increase in the MW of the macromolecules. However, this dependence is less pronounced, is observed in the region of low molecular weights, and is manifested against the background of a considerable scatter of experimental points.[44] Subsequently, direct experiment demonstrated[10,44] that the rates of diffusion of gases and solvents in polymers are determined by their number-average MW in conformity with the conclusions which follow from the free volume theory.

The question of the influence of the MW of macromolecules on the diffusion properties of polymeric media is in its theoretical aspect part of the more general problem of the contribution of the end units of macromolecules to the kinetic properties of polymeric bodies. One must distinguish two extreme cases: in the first, the free or "hot" ends of the chains are of decisive importance, while in the second fixed or "cold" ends are important. The first case obtains in systems with linear macromolecules and the second in systems incorporating three-dimensionally cross-linked structures. Whereas the free ends of the chains exert a perturbing influence on the conformational state of the segments of macromolecules, increasing their mobility and free volume, the fixed chain ends have the opposite effect.

Experimental studies on the molecular movements and the rates of diffusion of low-molecular-weight substances in cross-linked polymers have demonstrated unambiguously the retarding effect of the modes of the three-dimensional network on the mobility of the structural elements of polymer chains.[8,11,31,45] Evidently, for a quantitative description of the effect of cross-links on the parameters of polymer matrices and membranes, one can use the ideas concerning the local free volumes of the units and modes. Within the framework of this approach, the following expressions have been obtained:

$$\ln D = \ln D_\infty - \frac{B}{f_\infty} \cdot \frac{a' M_n^{-1}}{f_\infty - a' M_n^{-1}} , \quad (11)$$

$$\ln D = \ln D_\infty - \frac{B a'}{f_\infty^2} \cdot M_n^{-1} . \quad (12)$$

Eqn.(12) holds for $M_n \geqslant 8 \times 10^2$. Here B and a' are constants and M_n is the molecular weight between the nodes of the three-dimensional network. Eqn.(12) agrees with the empirical relation between D and M_n.[20,31] One should bear in mind that Eqn.(12) is valid only for sufficiently high M_n, typical for vulcanised elastomers, whereas Eqn.(11) is valid over the entire range of densities of three-dimensional networks, up to the values of M_n characteristic of resites, epoxides, and polyesters. Eqn.(11) can be extended also to the vitreous and crystalline states of three-dimensionally cross-linked polymers. The rate of diffusion can be related with the aid of Eqn.(11) also to the number of nodes in the three-dimensional network, the molecular parameters of the cross-linking agent, the content of the hardening agent, the radiation dose, and the kinetics of the process leading to the formation of networks.[7,20,46,47]

2. Diffusion in Static Copolymers and Polymer–Solvent 1–Solvent 2 Systems

The introduction into the polymer chain of units differing from the elements of the main chain in chemical composition, structure, and stereochemical parameters imposes a definite imprint on the molecular movement within the polymer systems, altering the rate of diffusion in them. In terms of the character of their behaviour, any polymer chains whose monomeric units differ in some way from one another can be included in the class of copolymers. However, the diffusion properties of copolymers cannot be described in a unique

fashion. This is because the properties of copolymers are determined not only by the concentration of units of different types but also by the character of their distribution along the chain, the stereochemical interaction, the phase structure of the system, and the nature of the solvent. It is therefore always essential to take into account the specific features of the real system investigated.

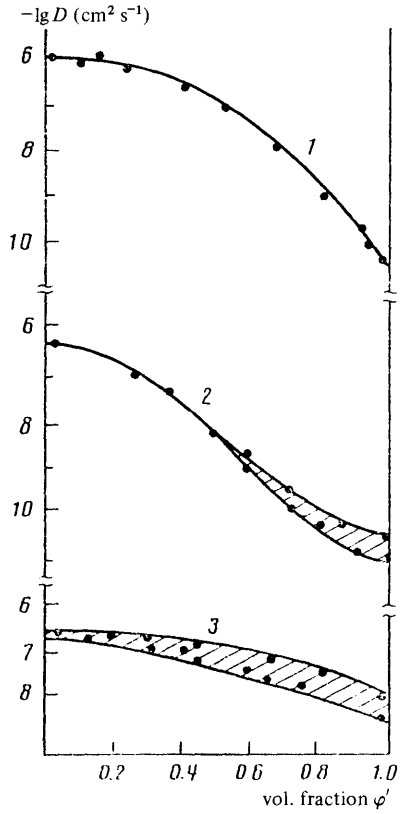


Figure 2. Dependence of the diffusion coefficients of low-molecular-weight substances on the composition of statistical copolymers: 1) styrene–butadiene copolymer in dibutyl sebacate (70 °C); 2) styrene–butadiene copolymer in benzene (25 °C); 3) vinyl chloride–vinyl acetate copolymer in water (20 °C).[9,31,92]

In this Section we shall consider the diffusion properties of single-phase amorphous statistical copolymers. Fig.2 presents typical dependences of the diffusion coefficients of low-molecular-weight substances on the composition of the copolymers. It can be seen that, for different states of the statistical copolymer, three types of dependence of D on φ' obtain (φ' is the volume fraction of the homopolymer units in the chain). If $T_{exp} > T_g$ (T_{exp} is the experimental temperature) for any composition of the copolymer, including homopolymers, then the decrease of D with increased presence in the chain of units which increase its kinetic rigidity is as a rule described by a smooth convex curve (curve *1* in Fig.2). The diffusion coefficients are in this case extrapolated from the average range of compositions of the copolymers to values corresponding to D in the homopolymers. If the diffusion medium is in the vitreous state ($T_{exp} < T_g$) for any composition of the copolymer, including homopolymers, then the overall tendency in the variation of D, mentioned above, persists but the dependence becomes less pronounced (curve *3* in Fig.2). This is caused by the insignificant change in D on passing from one homopolymer to another combined with the significant dependence of the absolute values of D on the previous thermal history of the specimens.[20,31]

The third type of dependence (curve *2* in Fig.2) is characteristic of systems in which the transition from the highly elastic to the vitreous state occurs for a definite composition of the copolymer ($T_g' < T_{exp} < T_g''$, where T_g' and T_g'' are the glass points of the homopolymers). In these systems, the dependence of D on φ' acquires an S-shaped character and the diffusion coefficients obtained by extrapolation from the range of compositions corresponding to the highly elastic state to the region of the vitreous state (D_{exp}) do not as a rule agree with the experimental values of D for the homopolymers. It has been suggested[46–48] that the ratio D_{exp}/D_{ext} be used as the coefficient of the structural non-equilibrium of the given copolymer or homopolymer.

According to Reitlinger's classification,[20] the polymer–solvent 1–solvent 2 systems belong to the class of polymer–liquid–gas systems. The inclusion of these systems in the group of statistical polymers may give rise to surprise. There are two reasons for such inclusion: firstly, the identity of the phase states of diffusion media of this type; secondly, the qualitatively identical effects of the copolymer units and the molecules of the dissolved liquids on the segmental mobility of the macromolecules and hence on the diffusion properties of the membranes.

The polymer–solvent 1–solvent 2 systems include two groups of three-component systems differing solely in the character of the distribution of one of the components in the polymer matrix. The first (and main) group comprises systems in which the polymer membrane is in contact with a mixture of two or more solvents which penetrate it simultaneously. In systems of the second group (plasticised and modified polymers, moistened polymers, and polymers saturated with the vapours of monomers, solvents, etc.[31,49]), one of the components was distributed in the membrane beforehand while the other participates in the transport process. Here it is significant that the concentration of the first component is kept constant throughout the process. Despite the different form of treatment of the mass transfer process kinetics in these systems, the self-diffusion coefficients of the low-molecular-weight substances in these media can be analysed within the framework of a single approach.[7,53]

Although there have been numerous experimental or, more precisely, technological studies of the permeability of polymer membranes to various mixtures of low-molecular-weight substances,[49,50] few investigations have been devoted to the kinetics of the transport and diffusion of individual components. Nevertheless, one can already claim unambiguously that the variation of the ratio of the components in the media in contact with the polymer membrane has little effect in the course of the process: the same sequence of partial fluxes is retained as for the individual components, but their absolute magnitudes and the diffusion coefficients found from the delay time for each partial flux (D_θ) change somewhat.[51] Under these conditions, a feature common to all mixtures is observed: the greater the content in the solution of the solvent diffusing at the lowest rate, the smaller the difference between the partial fluxes D_θ of the mixture components; the overall flux of the mixture as a whole has as a rule a value intermediate between the partial fluxes

of the individual components; the overall flux usually attains a stationary value when stationary transport of the component diffusion at the lowest rate is established.

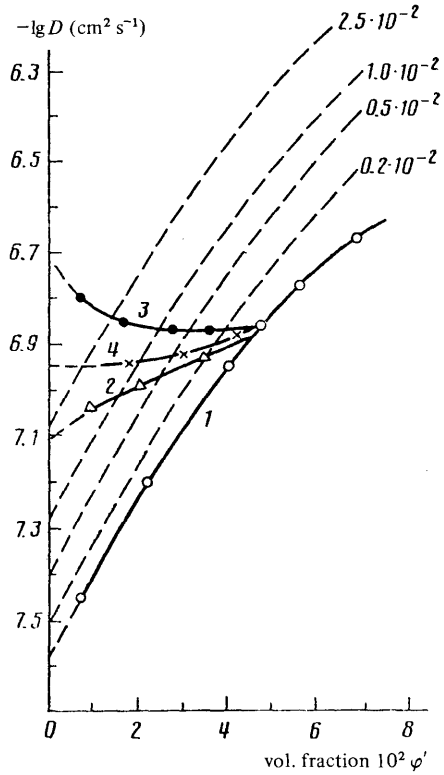


Figure 3. Dependence of the individual (curve *1*) and partial (curves *2*–*4*) diffusion coefficients of hexane in polyethylene on its content in various systems: 1) polyethylene–hexane; 2) polyethylene–hexane–pentachloroethane; 3) polyethylene–hexane–ethyl acetate; 4) polyethylene–hexane–cyclohexane. Dashed curves—theoretical relations calculated by Eqn.(14) for different contents of pentachloroethane in polyethylene (the numerals opposite the curves denote the concentrations φ'' in volume fractions).

The sequence of the permeation of the solvents through membranes affects the diffusion coefficients found along different sections of the non-stationary stage of the process. The variation of D_θ with the time of observation, described by Ferry,[51] is related to the mutual influence of the solvents in the course of their joint permeation. Special attention should be paid to the values of D_θ calculated in the initial stages of the permeation of the diffusants. Comparison of the partial flux D_θ of the solvent which diffuses first with its coefficient D_s calculated from the results of sorption measurements demonstrates their satisfactory agreement, while D_θ for the solvent diffusing after the first is higher, i.e. the effect involving the mutual plasticisation of the polymer membrane in the transport process takes place. Such effects are naturally not observed in the study of the kinetics of permeation and sorption (swelling) in systems of the second group.[48]

In the study of the characteristics of the diffusion and permeability of polymer membranes with respect to mixtures of low-molecular-weight substances, the composition of the solutions of the low-molecular-weight substances is usually employed as an independent argument. In our view, the use of the solubilities of the components in the polymeric medium as the independent variables is more promising for the analysis of the transport processes of multicomponent systems through polymer membranes. In this case, the experimental diffusion coefficients can be related to the concentration dependence of D in the polymer–diffusant binary system. Indeed, the partial diffusion coefficients of hexane diffusing from mixtures with different solvents have as a rule larger absolute values than in the polyethylene–hexane binary system (curve *1* in Fig.3). With increase in the concentration of hexane in the polymer (this corresponds to the increase in its content in the solution in contact), its partial diffusion coefficient can both gradually increase (curve *2* in Fig.3) and decrease (curve *3*) or can remain unchanged (curve *4* in Fig.3. However, and this is the most important factor, in all cases the partial concentration variations of D for this solvent approach the corresponding variations for the same component in the binary system. Extrapolation of the variation of the partial values of D to $\varphi_1 = 0$ makes it possible to find the diffusion coefficients of the given component in the matrix containing the maximum possible amount of the sorbed solvent 2. These values of D are specific to each polymer–solvent 2 system. As a rule, $D'' > D'$, where D' is the diffusion coefficient of solvent 1 in the polymer for $\varphi_1 = 0$ and D'' is the partial diffusion coefficient of the same solvent in the polymer saturated with solvent 2. The ratio of these diffusion coefficients can be used to estimate the plasticising effect undergone by the polymer matrix under the conditions of the simultaneous diffusion in the latter of the two solvents.

For three-component systems of the second group, analogous relations have been found experimentally. In this case, when a plasticising component is introduced into the polymer, the value of D for low-molecular-weight substances increases with increasing plasticiser concentration, as happens when copolymer units are introduced into the macromolecular chain. Only in isolated instances where the plasticiser reduces the segmental mobility, i.e. behaves as an antiplasticiser, do the diffusion coefficients of gases, water, and solvents diminish somewhat under these conditions.[52]

In order to interpret the results and to predict the diffusion properties of copolymers plasticised in three-component systems, one may use the expression

$$\ln\frac{D}{D'} = \frac{B}{f'}\left(\frac{\beta\varphi''}{f'+\beta\varphi''}\right) , \qquad (13)$$

$$\ln\frac{D}{D'} = \frac{B}{f'}\left(\frac{\beta_1\varphi_1''+\beta_2\varphi_2''}{f'+\beta_1\varphi_1''+\beta_2\varphi_2''}\right) , \qquad (14)$$

which follow from the classical free volume theory.[7] In Eqn.(13), D' is the diffusion coefficient of the test component in the homopolymer, f' its free volume fraction, φ'' the volume fraction of either the copolymer units or the plasticiser, $\beta = f' - f''$, and f'' is the free volume fraction either in the second homopolymer or in the plasticiser. In Eqn.(14), D' is the partial diffusion coefficient of the test component in the polymer, f' its free volume fraction, $\beta_1 = f_1'' - f'$, and $\beta_2 = f_2'' - f'$, where f_i'' is the free volume fraction in each solvent, φ_i'' the volume fraction of the corresponding solvent, and B are constants. The results of the calculation by Eqn.(14) for the polyethylene–hexane–pentachloroethane system are presented in Fig.3 in the form of dashed lines (each dashed line corresponds to a specific value of D for pentachloroethane). It can be seen that the

experimental curve for the partial diffusion coefficients (curve *2*) intersects the theoretical relation at certain points corresponding to the average values of D for the given composition of the polymer–solvent 1–solvent 2 system. In recent years, this method has been developed further.[53]

3. Diffusion in Polymeric Glasses

It has been shown in a whole series of experimental studies[3,5,6,9] that, when $T < T_g$, the mass transfer of low-molecular-weight substances in polymeric diffusion media cannot be described using solely the molecular characteristics of the macromolecules. The activation energy for the diffusion of low-molecular-weight substances in polymeric glasses is as a rule lower than in the highly elastic state of the same medium. Admittedly, for certain diffusants, usually helium and hydrogen, these differences do not exist. For the same diffusant, the quantity E in the polymeric glass is a function of the excess free volume: the greater the latter, the smaller the value of E. A linear realation is observed between the diffusion coefficients of the low-molecular-weight substances and the densities of the glasses ρ and the latter vary comparatively little; for example, $\lg D = 8.2 - 14.5\rho$ ($1.19 \leqslant \rho \leqslant 1.23$ g cm^{-3}) for the diffusion coefficients of water in hardened epoxide resins.[46]

All these facts led many investigators[55–58] to turn to a more detailed consideration of the structure of the polymeric glass and to the study of the characteristics of mass transfer at $T < T_g$.

In our view, there are no fundamental differences between the mechanisms of the diffusion of fairly large molecules of low-molecular-weight substances in polymeric media at temperatures below and above T_g: in both cases the vibration of the diffusing molecule takes place as a result of the appearance near it of a microcavity vacancy of the appropriate size. The number of vacancies per unit volume depends in the general case on temperature, the packing density of the macromolecules, pressure, the content of modifying agents, etc. Thus one can assume that the principal relation (2) of the free volume theory is valid also for polymeric glasses.

According to this approach, the difference between the states of the polymer matrix above and below T_g is associated with the fact that the thermal movement of the structural elements of the macromolecule, responsible for the diffusional migration of the low-molecular-weight substances, takes place under these conditions for different supermolecular organisations of the medium. At $T > T_g$, the diffusion process takes place in a medium with an equilibrium or nearly equilibrium packing of the chains ($f = f_t$, where f_t is the free volume fraction associated with the thermal expansion of the matrix), whereas at $T < T_g$ the process takes place under the conditions of a non-equilibrium albeit quasi-stationary structural organisation of the matrix, for which $f > f_t$. It is natural to assume that in the latter case $f = f_t + f_v$, where f_v is the free volume fraction association with the non-equilibrium nature of the matrix, the so called excess free volume. Evidently, f_v is the "frozen" free volume determined by the non-equilibrium nature of the structure and the relaxation nature of the vitrification process. It is determined by the previous history of the specimen, whereas f_t is determined by its chemical nature, composition, and external conditions. One may say that f_t is the level of defectiveness of the structure against the background of which the effect of f_v is manifested. The fact that f_t plays a definite role also at $T < T_g$ is indicated by relaxation spectrometric data.[54,60,61] Since the diffusion coefficients of low-molecular-weight substances in polymers are an integral characteristic of the mobility of the macromolecular fragments, the nature of these elements and their concentration must inevitably influence the mass transfer process also at $T < T_g$. At any rate, a whole series of properties of polymeric glasses exhibit a dependence on the molecular characteristics of the system, which although weak is nevertheless explicit.[61]

Unfortunately, neither the vacancy solution model, nor the Simha–Boyer model, nor the results of experiments on the annihilation of positrons[62,63] permit an unambiguous differentiation of the contributions to f by f_t and f_v. Attention is therefore concentrated nowadays on the search for direct correlations between the diffusion permeability constants, on the one hand, and the results of structural studies on the other. The equation

$$\ln \frac{D}{D_s} = \frac{B}{f_s}\left[\frac{(1-f_s)(1-\rho/\rho_s)}{(1-f_s)\rho/\rho_s - 1}\right] \qquad (15)$$

has been obtained[7,46] within the framework of the free volume theory. For a narrow range of variation of the density of the polymer matrix, it can be put into the simple form

$$\ln D = \alpha - \gamma\rho \qquad (16)$$

It relates the diffusion parameters to an integral structural characteristic of the polymer ρ, namely its density, and agrees well with experimental data. In Eqns.(15) and (16), α and γ are constants and ρ_s, f_s, and D_s are respectively the density, the free volume, and the diffusion coefficient of the polymer in a selected standard state (for example, at T_g).

The experimental data accumulated to date on the diffusion absorption of gases and solvents in polymeric glasses and the permeability to these substances are consistent with the qualitative structure of the model. The vacancies constituting the free volume are combined into vacancy capillaries with a variable radius and a thermally fluctuating wall, i.e. one which constantly alters the "frozen" average size of the vacancy capillary. The size of the vacancy capillary (its average radius and the radii at the narrowest and widest points) is determined by the parameters of the vacancies at $T > T_g$.[33,34] The thermal mobility of the macromolecular fragments at $T < T_g$ (i.e. f_t) is localised in the outer layers of the capillary and is independent of its size. Hence it follows, for example, that E and the character of the mass transfer process depend on the ratio of the average vacancy diameter $\bar{X}$ and the diffusant diameter d. Evidently, the greater the value of $\bar{X}$, the smaller that of E. For certain values of $\bar{X}$, the quantity E, measured at a temperature above T_g, is equal to the activation energy for diffusion in the vitreous state. For $\bar{X} \gg d$, there is a possibility of a non-activated mechanism of gas permeability.[20,31] If this model is adopted, then, in order to create highly productive and selective membranes, one must use polymers whose macromolecules are separated from one another by a fairly large distance and which have large groups characterised by a high effective modulus of the bending of the chain and which also contain mobile fragments. An indirect confirmation of this model is probably provided by data for gas separation on polytrimethylsilyl-propyne.[64]

IV. DIFFUSION IN HETEROGENEOUS SYSTEMS

A fairly large group of polymer systems belongs to the class of heterogeneous diffusion media: crystalline homopolymers and copolymers, polymer blends and block copolymers, filled and gas-filled polymers, multilayer and combined film materials, protective

coatings, and membranes, i.e. one-component or multicomponent systems which exist under the experimental conditions in two-phase or multiphase states. The study of diffusion processes in these systems is prosecuted nowadays in three directions. In the first place, a detailed study is made of translational diffusion processes involving the components or macromolecular fragments responsible for the formation of the phase structure of these media. This aspect of the problem has been analysed in detail in relation to a whole series of binary polymer systems: reactive oligomer–elastomer systems,[65,66] gas-filled elastomers and plastics,[7,67] the formation of a porous structure,[68] and the growth of the particles of the disperse phase in the metastable and labile regions of the phase diagram.[69,70] The second direction is associated with the study of the role of diffusion processes in the formation of transitional zones in multilayer systems.[71] The third direction combines studies on the diffusion properties of heterogeneous polymeric media, mainly in relation to gases, water, organic solvents, electrolytes, monomers, etc.

Despite the fact that the first two directions are closely related to mass-exchange processes between individual phases in heterogeneous systems, this relation is mainly terminological. To a large extent, they are associated with mutual diffusion and self-diffusion processes in various zones of the phase diagram, on the one hand, and with the phase decomposition kinetics, on the other. We shall therefore deal here only with the studies of the diffusion of low-molecular-weight substances in heterogeneous polymeric materials.

Following Chalykh,[7] we shall divide all heterogeneous polymer systems into two large groups. In the first group, we shall place systems whose disperse phase does not participate in the sorption and diffusion processes involving low-molecular-weight substances and influences them only indirectly by acting on the density and segmental mobility of the chains in the dispersion medium. This group includes crystalline polymers, melts comprising crystalline polmers with elastomers and thermoplastics, and polymers filled with mineral powders or fibres. The second group is made up of systems whose disperse phase and dispersion medium participate simultaneously in the sorption, diffusion, and permeation processes. Mixtures of amorphous polymers, block copolymers, and gas-filled systems belong to this group.

1. Diffusion in Systems with Impermeable Particles of the Disperse Phase

It has been demonstrated convincingly by X-ray diffraction that the crystalline phase of the majority of synthetic and natural polymers is impermeable to the molecules of various diffusants. Systems in which the diffusants form solvates with the macromolecules, clathrate complexes, or molecular complexes should probably be exceptions.[72] However, there is so far no information about the translational diffusion coefficients in such phase formations.

The diffusion low-molecular-weight substances in partly crystalline polymers has now been studied in greatest detail.[1,6,7,20,31] Nevertheless, the following main problem still remains open: what is the relation between the supermolecular and phase organisations of these polymers, on the one hand, and the translational mobility of the low-molecular weight substances dissolved in it, on the other. The crystallite is usually employed as the structural element constituting the diffusion medium and the diffusion and permeability coefficients are related to the degree of crystallinity φ_c, using for this purpose empirical or semiempirical relations:

$$D = D_a(1-\varphi_i)^n; \quad P = P_a(1-\rho)^m \quad , \tag{17}$$

$$D = D_a \exp\left(-\frac{B}{f_a}\cdot\frac{\varphi_c}{1-\varphi_c}\right) \quad , \tag{18}$$

$$D = D_a(\tau\beta)^{-1} \quad . \tag{19}$$

where D_a is the diffusion coefficient of low-molecular-weight substances in the amorphous phase or in the amorphous analogue of the crystalline polymer, P_a the permeability coefficient of the same media, τ the tortuosity factor of the pathway, β the immobilisation factor of the crossing chains, f_a the fraction of free volume in the amorphous phase of the polymer, and n, m, and B are empirical constants. It has been shown in a number of studies that n varies in the range from 1.3 to 2.[7,20,31] According to self-diffusion data, $n = 8$.[73]

Another view has been expressed in a number of studies[74–76] whose authors suggest that the diffusion properties of crystalline polymers are determined by their spherulitic level and that the variation of D and P should be attributed not to the variation of φ_c but to the variation of the "degree of spherulitic character". This approach is based on two groups of experimental results; firstly, there are autoradiographic data, according to which the transport of the diffusant in coarsely spherulitic specimens takes place along the boundaries of the spherulites and, secondly, the results of numerical calculations of the permeability coefficients, according to which the peripheral regions of the spherulites are more permeable than their middle section. However, it has been shown for the majority of crystalline polymers that the variation of the size of the spherulites Φ from 2 to 40 μm for film thicknesses in the range 150–300 μm does not affect D and P. An increase in D and P has been observed only for values of Φ comparable to the thickness of the membranes, whereupon breaks in continuity within the spherulites and along their periphery go right through these formations. Therefore one should probably not use the spherulitic level as the cornerstone it being more useful to treat the problem in terms of the spectrum of translation pathways localised both in the intercrystallite and interspherulite spaces, differing from one another in tortuosity, in the packing density of the crossing chains, and in the number of defects.

This problem has been solved[77] within the framework of the permeation theory. It was assumed that the problem of mass transfer in partly crystalline polymers can be formalised as the problem of nodes whose size is much smaller than the thickness of the membrane. A node is permeable when it contains the amorphous phase and is impermeable when it contains a crystallite. Diffusion in such a system occurs only when the fragments of the permeable phase form an infinite cluster, i.e. when the content of the amorphous phase exceeds the permeation threshold φ_a^c, which is 0.16 for the model considered. Using the relation between the tortuosity of the infinite cluster and the fraction of the permeable nodes[78] $\tau \propto (\varphi_a - \varphi_a^c)^t$, where t is the critical index which varies from 1.6 to 2 (the space is three-dimensional) and Eqn.(15), one can obtain the expression

$$D = D_a(\varphi_a - \varphi_a^c)^t \quad , \tag{20}$$

which describes satisfactorily the experimental data over a fairly wide range of variation of the degree of crystallinity of the polymers. It is noteworthy that the critical index is extremely sensitive to the molecular weight, the MWD, the composition of the macromolecules, and the degree of branching of the latter.

However, there exists a fairly large group of experimental data which indicates an anomalous variation of the diffusion properties of crystalline polymers: an increase in D and φ_a with increase in φ_c, the variation of the critical index for φ_c = const., and the decrease in the activation energy for diffusion with increase in φ_c. These results (Fig.4) have been obtained as a rule for high degrees of crystallinity in the vicinity of φ_a^c. The rate of increase in D with increase in φ_c can vary. For some specimens, an almost abrupt increase in D is observed, for others, a more common case, there is a gradual increase, and for the third group, D = const. This character of the variation of D with φ_c has been attributed[58,79,80] to the decrease in the immobilisation factor of the crossing chains. This effect has been explained[7] by the variation of the chain packing density ρ_a in the amorphous phase.

The anomalous variation of D can be explained analogously also within the framework of the percolation approach. Indeed, we shall begin with the hypothesis that the tortuosity of the transport channel increases with increase in φ_c in accordance with Eqn.(20). Then all the structural changes occurring within the channel must be reflected in D_a. Fig.4 shows that most of the experimental data for this range of values of φ_c occupy an intermediate position between two curves calculated by Eqn.(20) for $D_a = 10^{-7}$ cm^2 s^{-1} and for $D_a = 10^{-3}$ cm^2 s^{-1}. The first value corresponds to the diffusion coefficient of the low-molecular-weight substance in the amorphous analogue of the polymer, for example, polyethylene, while the second corresponds to the diffusion coefficient of the same diffusant but in the gas phase, where the transport channel is identified with a crossing pore having Knudsen dimensions.[81]

Evidently, there may be several versions of structural organisation for the transport channel in real materials: the appearance within the channel of local breaks in continuity—closed pore and microcracks; an inhomogeneous distribution of density along the channel cross-section; a general decrease in the density of the amorphous phase. Calculations have shown that, when the first version of the channel structure obtains, a deviation from the theoretical relation (20) is observed only for $\varphi_c \geqslant 0.7$ (curve *9* in Fig.4), i.e. virtually near the permeation threshold. The appearance in the channel of defects of the second type leads to an abrupt alteration of D and its subsequent decrease with increase in φ_c (curve *7* in Fig.4). Finally in the third case D = const., or a weak increase in D, or sharp increase with increase in φ_c can be attained depending on the character of the variation of φ_c (curve *8* in Fig.4). Comparison of these results with experimental data shows that the formation of the transport channel with the first and third versions of the defective structure is more realistic under normal crystallisation conditions.

In the case of crystallisable copolymers and comb polymers, their diffusion properties in each specific case are determined by the coefficient D of the low-molecular-weight substances in the homopolymers, the composition of the crossing chain, the kinetic mobility of the segments, and the degree of crystallinity. An attempt to predict the diffusion properties of crystalline variable-composition copolymers has been undertaken[7,84] within the framework of the free volume theory and the statistical theory of the crystallisation of copolymers.[85] It has been shown that account must be taken of at least three variable parameters for the description and prediction of their properties: φ_c, the composition of the crossing chains, and the

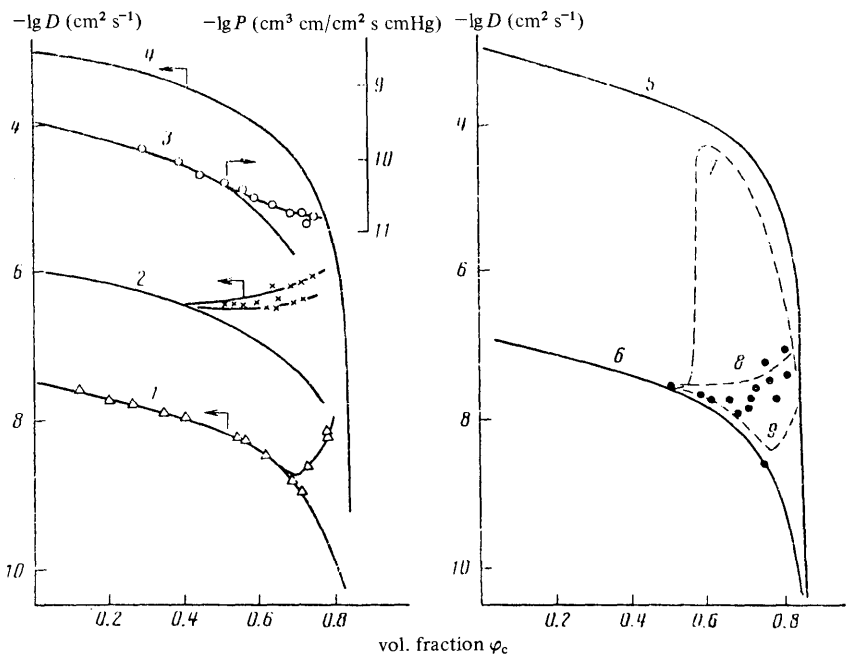


Figure 4. Dependence of the diffusion and permeability coefficients of low-molecular-weight substances on the degree of crystallinity of the polymers: 1) polypropylene–hexane; 2) polyethylene–methane; 3) polyethylene–nitrogen; 4) and 5) calculation by Eqn.(20) for $D_a = 10^{-3}$ cm^2 s^{-1}; 6) calculation by Eqn.(20) for $D_a = 10^{-7}$ cm^2 s^{-1}; 7)–9) calculation by Eqn.(20) for different models of the structure of the amorphous phase (for explanation, see text).

distance of the system from the permeation threshold. Analogous calculations can probably be performed also with the aid of Eqn.(20).

For amorphous polymers filled with the impermeable particles of a disperse phase with a different chemical nature, it is also possible to differentiate three regions of the degree of filling (φ_f) in which the diffusion parameters depend on φ_f in different ways: the region $\varphi_f \leqslant 0.10$ where the introduction of the filler decreases D and P; the region $\varphi_f > 0.20$ where as a rule D and P increase with increase in φ_f; the region of middle compositions of disperse systems where both the constancy of D and P and their extreme changes can be observed as a function of the nature of the polymer and the filler. Thus the general tendency in the variation of the diffusion properties of filled polymers is analogous to that described above for crystalline polymers. The specific features of filled systems are manifested by the fact that all the phenomena described occur in a comparatively narrow range of the bulk phase content of the disperse phase particles. The few structural-morphological studies on these systems have shown that the deviations from Eqn.(20) are associated, on the one hand, with the flocculation of the particles of the disperse phase to give chain cluster formations, and, on the other hand, with the formation of defects—local breaks in continuity concentrated either at the interface or within the cluster structures. Direct evidence for the formation of such structures has been obtained in a study of the gas permeability of porous membranes formed by filling elastomers with powdered salts and their subsequent elution.[86] The formation of crossing porosity has been noted[87] already at $\varphi_f \cong 0.05$.

In conclusion of this Section, we may note that, despite the large amount of experimental data on diffusion in filled polymers and on their permeability, they still remain the least investigated. This is due to the virtual lack of combined studies in which diffusion data would have been supplemented by structural-morphological information, the determination of local diffusion coefficients, and the estimation of the degree of defectivness of the medium. The study[88] in which the percolation approach was used to analyse mass exchange processes in multicomponent polymer coatings is not an exception in this sense.

2. Diffusion in Block Copolymers, Polymer Blends, and Gas-filled Polymers

Assessment of the set of experimental data obtained for the diffusion behaviour of media containing a permeable disperse phase permits the conclusion that the behaviour of these systems shows no fundamental qualitative and quantitative differences despite the significant difference in the chemical and phase states of the particles of the disperse phase, their disperse characteristics, structural organisation, and local diffusion coefficients. When the disperse phase is impermeable to low-molecular-weight components for thermodynamic reasons, the diffusion properties of all these media are characterised by a single transport or macroscopic diffusion coefficient, while the sorption and permeation kinetics are of the normal, Fick type. On the other hand, if both the disperse phase and the dispersion medium are involved simultaneously in the diffusional transport of low-molecular-weight substances, then distinct pseudo-normal sorption and permeation kinetics are observed,[7] while the diffusion properties of the system are characterised by local and effective diffusion coefficients. The reproducible anomaly in the kinetics of the attainment of sorption equilibrium observed in these polymers after repeated sorption–desorption cycles yields direct information about the disperse structural organisation of the medium. The diffusion properties of such media are influenced by the differences between the diffusion coefficients of low-molecular-weight substances in the disperse phase and the dispersion medium. Since D for organic solvents is a function of concentration,[91] it is frequently found that in one region of sorption isotherms the medium is "heterogeneous" according to diffusion data while in another it is "diffusionally homogeneous".

The dual character of the behaviour of polymer media containing permeable particles of the disperse phase is also manifested when diffusion coefficients measured by different methods are compared. Thus the rotational and translational diffusion coefficients of iminoxy-radicals, found by microwave spectroscopic methods (D_R), exceed the corresponding coefficients of translational mobility obtained by sorption–permeability methods (D_S).[42] Whereas D_S diminishes with increasing content of the disperse phase, D_R = const.

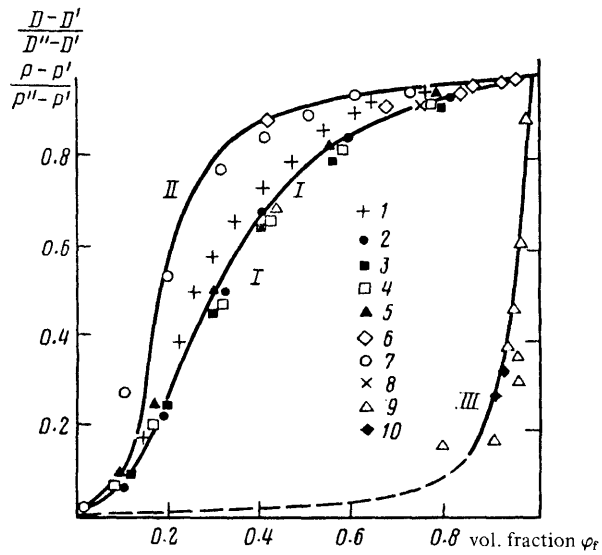


Figure 5. Dependence of the reduced diffusion coefficients of low-molecular-weight substances (I) and of the reduced permeability coefficients of heterogeneous polmeric materials (II) as well as gas-filled polymeric systems obtained by sintering (II) and foam formation (III) on the porosity and content of the permeable phase: 1) "Silar" poly(block copolymer); 2) polystyrene–polybutadiene blend; 3) styrene–butadiene block copolymer; 4) sulphone–butadiene block copolymer; 5) blend of poly(vinyl chloride) and nitrile rubber; gas-filled polymers; 6) SKN-30 nitrile rubber (elution of KCl); 7) polyurethane (sintering of particles); 8) polyamide fibres (unwoven material); 9) polyester-urethane foam; 10) polystyrene foam; D, D', and D'' are the diffusion coefficients and P, P, and P'' are the permeability coefficients of the mixture and of each pure components respectively; φ_f is the content of the permeable phase (in the case of gas-filled polymers, it is their porosity).

Fig.5 presents experimental reduced diffusion and permeability coefficients for many polymeric media with a permeable disperse phase. Curves illustrating the variation of the permeability of gas-filled polymer systems obtained by sintering powders and by foam formation are presented for comparison.[89,90] For all the systems, the

character of the variation of the effective coefficients D and P is the same. In the region of phase reversal (which occurs in the vicinity of the permeation threshold when the problem of nodes in a lattice-free model is considered), D and P undergo the greatest changes. The critical index t is close to 1.7 even for gas-filled systems. The dependence of the permeability coefficients on the porosity—the volume fraction of the permeable phase for polymeric foam materials—is of special interest. Despite the fact that the content of gas inclusions reaches up to 93 vol.%, the permeation threshold in this system has not been attained. These results can be explained within the framework of the problem of connections.[90] The accumulation in the specimen of pore walls disrupted by influences of one kind or another leads to the formation of passable connections between the lattice nodes and to the appearance of an infinite cluster, which is manifested by a sharp and abrupt increase in gas permeability.

Several approaches have been proposed for the theoretical study of the diffusion of low-molecular-weight substances in heterogeneous polymer systems with a permeable disperse phase: the Maxwell, Nielson, and Robinson equations, the Zolotarev–Dubinin bidisperse model, and the percolation model. It is necessary to compare the proposed equations, to determine their scope in predicting the behaviour of heterogeneous diffusion systems, and to estimate the structural-morphological features of the test objects. First attempts of this kind have already been undertaken.[7,88,91–93]

V. DIFFUSION METHODS FOR THE STUDY OF POLYMER SYSTEMS

1. Construction of Phase Diagrams

The diffusion methods for the study of polymer systems are based on the investigation of the concentration distribution of the components in the mutual diffusion zone, i.e. in the zone corresponding to the spontaneous mixing of the components. At the present time, it has been demonstrated for various systems that the characters of the concentration profile and of the phase diagram for the system are closely interrelated (Fig.6). Thus, if the polymer system is characterised by amorphous layer formation and exists during the experiment above the upper consolute temperature (UCT) or below the lower consolute temperature (LCT), then the distribution curves indicate a continuous variation of concentration on passing from one component to another. At T < UCT (or T > LCT), a concentration jump is observed on the diffusion profiles, whose position corresponds to the two-phase region on the concentration scale of the phase diagram. The composition of the solutions on either side of the phase boundary then coincides with the composition of the

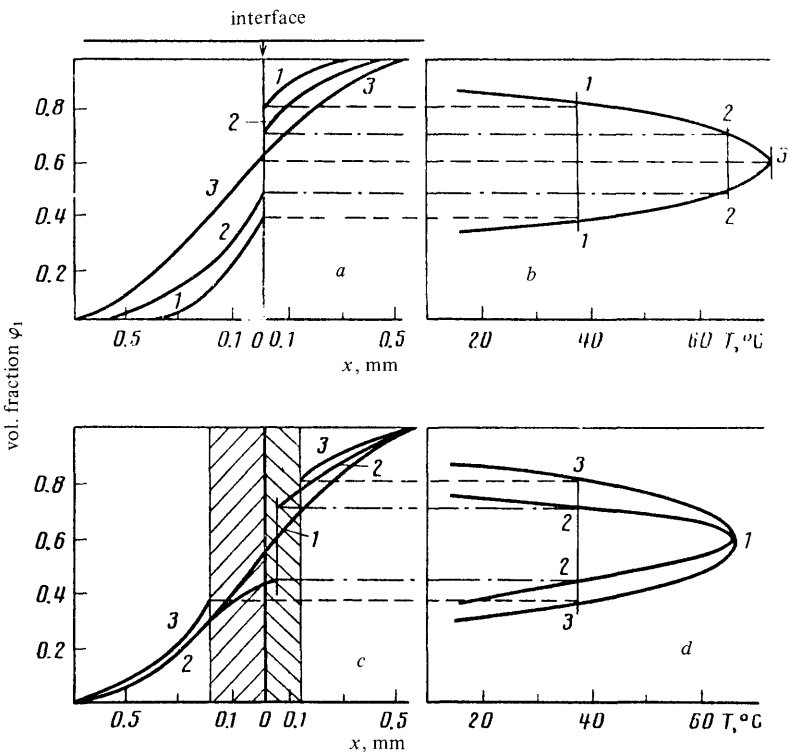


Figure 6. Concentration distribution curves in the mutual diffusion zone (*a*, *c*) and the phase diagrams (*b*, *d*) constructed on their basis. Curves *1*–*3* corresponding to increasing (*a*) and decreasing (*c*) temperatures; the boundary concentrations on curves *2* and *3* (*c*) correspond to the spinodal and binodal curves. The phase decomposition regions are shown cross-hatched; x is the diffusion coordinate.

coexisting phases. Thus, by determining the variation of the boundary concentrations at different temperatures and the instant of disappearance of the interface, one can plot, as shown in Fig.6, the binodal curve of the phase diagram.

If the binary system is characterised by a crystalline equilibrium (in the general case by a combination of crystalline and amorphous equilibria), then the distribution of concentration in the mutual diffusion zone includes additional regions corresponding to the dissolution of the diffusant in the crystalline polymer and its fusion if the dissolution takes place at $T < T_m$ [T_m is the melting point]. In order to characterise this region, it is necessary to identify experimentally the amorphous and crystalline states of the solutions. For example, when measurements are performed by the interference or polarisation-interference methods, the concentration profiles must be recorded in both ordinary and polarised light.[94]

An inherent feature of the diffusion method for the construction of phase diagrams is the possibility of determining the spinodal curve and also of the kinetics of phase decomposition in the region of metastable and labile solutions.[95] For this purpose, the diffusion process is carried out initially under conditions such that a concentration field arises in the miscibility zone and the range of variation of the composition of the solutions must be fairly broad. By driving the system as a result of a sharp change in temperature to the region of phase separation, it is possible to observe and record different stages in the decomposition of labile and metastable solutions. By determining under these conditions the boundary concentrations, established at different times near the phase boundary, one can plot (Fig.6) the spinodal curve, test the position of the binodal curve, and determine the concentration-temperature range corresponding to phase reversal. These methods are of great practical interest, because it is precisely under these conditions (i.e. in the presence of the concentration or diffusion coefficient gradient) that the stuctures of coatings, membranes, and adhesion junctions are established.

2. Phase and Structural Analysis of Polymer Blends and Block Copolymers

The phase and structural analysis of heterogeneous polymer systems presupposes the determination of quantitative information about the phase composition of the specimen, the size and shape of the particles of the disperse phases, the compositions of the coexisting phases, and the size and structure of the interfaces. Detailed investigations of various aspects of mass transfer process involving low-molecular-weight substances in such systems have shown that the characteristic features of their phase state and supermolecular organisation are most strikingly manifested in the kinetics of the attainment of sorption equilibrium.[13,91,98]

The kinetics of the sorption (desorption) of solvents by block copolymers and polymer blends are characterised by a series of specific features, which make it possible to differentiate them as a special class of heterogeneous sorbents. In the first place, the type of kinetic curve depends on the nature of the sorbate and its thermodynamic affinity for the blocks forming the disperse phase and the dispersion medium. Thus, when a selective solvent (SS) which is not sorbed by the disperse phase is used as the sorbate and the dispersion medium is in the highly elastic state, then the sorption kinetics are as a rule of the normal, Fick type. The situation is different if the sorbate is a common solvent (CS) for both phases. In this case, the type of the kinetic curve depends on how much the diffusion coefficients of the sorbate in the disperse phase (D') and in the dispersion medium (D'') differ.

The diffusion in such systems can be naturally characterised with the aid of models taking into account the phase structure of the sorbent, for example, with the aid of the bidisperse Zolotarev–Dubinin model. Two diffusional relaxation times have been introduced in this model: $T = \Gamma L^2/D''$ for the dispersion medium and $\tau = R^2/D$ for the disperse phase. Here L and R are the sizes of the specimen and the phase inclusion respectively and Γ is the Henry coefficient. Depending on the ratio of T and τ, the following cases can obtain: for $T \gg \tau$, the rate of sorption and the type of kinetics are determined by the transport in the dispersion medium; for $T \ll \tau$, the sorption kinetics are determined by the diffusion initially into the dispersion medium and then into the disperse phase and there is a possibility of both two-stage and pseudo-normal kinetics; for $T \cong \tau$, an intermediate case arises; when $\tau \to \infty$, normal sorption, involving the transport of the test substance in the dispersion medium, takes place. Thus, having determined from the experimental data for the sorption kinetics the values of T and τ and having assumed that the diffusion phase coefficients in the disperse phase and in the dispersion medium are close to the diffusion coefficients of the corresponding homopolymers, it is possible to estimate the average sizes of the particles of the disperse phases.

Several methods have been proposed for carrying out calculations of this kind.[13] The most rational procedure for the treatment of kinetic sorption curves has been described in a study[99] whose authors derived simple relations between the principal process characteristics by the numerical calculation of various linear and concave sorption isotherms for sorbents with a bidisperse structure:

$$\gamma(t) = 1 - \exp\left\{A(\varepsilon)\left(\frac{t}{\tau+T}\right)^{B(\varepsilon)}\right\} \qquad (21)$$

where γ is the relative degree of filling of the sorbent by the sorbate, t the time, $\varepsilon = \tau/(\tau + T)$, and $A(\varepsilon)$ and $B(\varepsilon)$ are empirical coefficients which depend on the form of the disperse phase. Their numerical values have been published.[99] These analytical formulae can be used to find from the experimental curves both D' and D'' and the corresponding diffusion relaxation times and hence also certain structural parameters of the medium. It is significant that this method does not require the knowledge of the entire sorption curve.

3. Determination of the Thermodynamic Parameters of the Mixing of the Components

New possibilities for the determination of the chemical potentials of the components in solutions of polymers (μ_i) are provided by the method of non-equilibrium thermodynamics, which makes it possible to relate in a fairly general and clear form the mutual diffusion and partial self-diffusion ($D^*_{i,\varphi}$) coefficients of the components to the thermodynamic characteristics of the solutions:

$$D_V = D^*_{i\varphi}\frac{\partial \ln a_i}{\partial \ln \varphi_i} = D^*_{i,\varphi}\frac{\varphi_i}{RT}\frac{\partial \Delta\mu_i}{\partial \varphi_i} \quad , \qquad (22)$$

where a_i is the activity of the ith component and φ_i its volume fraction. It follows from Eqn.(23) that

$$\Delta\mu_i = RT\int_1^{\varphi_i}\left(\frac{D_V}{D_{i,\varphi}}\right)\varphi_i^{-1}\,d\varphi_i \qquad (23)$$

Eqn.(23) makes it possible to determine the change in the chemical

potential of any component of the diffusion system.[7,100] The calculations can be performed in accordance with the following scheme: initially, one determines experimentally the concentration dependence of D_V and then also experimentally or by calculation, using the Fujita equation, one finds the concentration variation of the partial self-diffusion coefficient of the ith component. Next $D_V/D^*_{i,\varphi}$ is plotted against $\ln \varphi_i$, graphical integration is carried out, and finally $\Delta\mu_i$ is determined by Eqn.(23). The subsequent treatment of the $\Delta\mu_i - \varphi_i$ relation in order to obtain the Gibbs free energy is traditional.[101]

It has been suggested[7] that the concentration variations of D_V and D^*_i be used to determine the interaction parameters χ characterising the thermodynamic affinity of the components in the Flory–Huggins theory. For this purpose, one can use the equation

$$D_V = D^*_{i,\varphi}\left[1 - \left(1 - \frac{V_1}{V_2}\right)\varphi_1 - \chi 2\varphi_1\varphi_2\right] , \qquad (24)$$

where V_1 and V_2 are the molar volumes of the components and φ_1 and φ_2 are their volume fractions. For polymer–low-molecular-weight substance systems with $V_1 \ll V_2$, this relation assumes the form

$$D_V = D^*_{i,\varphi}(1 - \varphi_1 - 2\chi\varphi_1\varphi_2) . \qquad (25)$$

If one uses the relative diffusion coefficient D_1, then, instead of Eqn.(25), one can obtain the simplest expression for the calculation of χ in a binary polymer system:

$$D_1 = D^*_1(1 - 2\chi\varphi_1) . \qquad (26)$$

Thus, both in the determination of $\Delta\mu_1$ and $\Delta\mu_2$ and in calculations of χ, it is essential to have information about the concentration variations of D_v and D^*_i. The integral values of χ can be estimated by means of extrapolated values of $D_{11}(\varphi_1 \to 1)$ and D^*_{11}, because $D_{11}/D^*_{11} = 1 - 2\chi$. The errors in the determination of $\Delta\mu_i$ and χ are related mainly to the error in the measurement of the mutual diffusion and self-diffusion coefficients and amount to ~15%.

4. Structural Studies on Crystalline and Filled Polymers

It is possible to differentiate several structural-morphological levels in these systems. The first is associated with the organisation of the crossing chains in the amorphous phase and determines its density, the distribution of density on passing from one crystallite to another, and the positions of the end groups and folds. The second has a bearing on the relative positions of the crystallites in space, their size, character, aggregation, internal structure, and degree of defectiveness. The third, superspherulitic level determines the character of the packing of the spherulites and their interrelation and internal structure. This structural hierarchy can be extended also to filled polymers after the introduction of the corresponding terminological refinements. Thus the amorphous phase of crystalline polymers is identical with the polymeric dispersion medium, the second level determines the distribution of the particles of the disperse phase, and the third determines the distribution of aggregates of the filler particles.

Analysis of experimental data has shown that the results of diffusion measurements make it possible to characterise to some extent each of the above structural-morphological levels. However, we believe that it is most useful to employ diffusion measurements for the study of the structure of the amorphous phase of crystalline polymers.

It has been suggested[58,80] that diffusion methods be used for the structural analysis of crystalline polymers. However, the authors confine themselves to the establishment of qualitative relations between the diffusion coefficients and the structural parameters of the media determined by other methods. This approach cannot be regarded as a method of structural analysis, because it reduces essentially to the solution of the converse problem—the use of information about the structure of the specimens for the interpretation of the results of diffusion measurements.

As already mentioned above, the application of diffusion methods in structural analysis presupposes something different: the determination of quantitative analytical relations between the diffusion constants and the structural characteristics of crystalline and filled polymer matrices. If Eqn.(18) is used for this purpose, then, when information is available about D and D_a, it is possible to estimate φ_c, and, when D and φ_c data are used, one can calculate the density of the amorphous phase in real polymeric materials. These estimates can be performed with the aid of the equation

$$\frac{\rho}{\rho_a} = \frac{\rho_c}{\rho_a}\left(1 - A + \frac{\rho_a}{\rho_c}A\right) , \qquad (27)$$

where ρ_c, ρ_a, and ρ are respectively the densities of the crystallites, the amorphous analogue, and the amorphous phase of the real polymer, $A = \ln(D/D_a)/\ln(D_{calc}/D_a)$, D_a and D are respectively the diffusion coefficients of the low-molecular-weight substances in the amorphous analogue and in the real polymer, and D_{calc} is the diffusion coefficient calculated by Eqn.(18) from D_a, f_a, and φ_c. On passing to filled polymers, the approach remains the same and only the physical significance of the symbols in Eqn.(27) changes.[7]

In this Section, we have considered certain possibilities in the application of diffusion methods to the physicochemical analysis of polymer systems. It is to be expected, that, as the methodological, molecular-kinetic, and phenomenological approaches are perfected, these possibilities will expand and will find an honourable place among other integral methods for the analysis of real polymeric materials.

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Molecular-kinetic Models of the Transfer of Substances in Inorganic Membranes

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Molecular-kinetic models of the transfer of susbstances through crystalline inorganic membranes have been examined, taking account of the influence of the principal real properties of the system: the interaction between the particles adsorbed on the surface and between the particles dissolved in the volume of the membrane; the non-uniformity of the region of the solid next to the surface; the restricted mobility of the particles; and the change in the state of the volume phase during the transfer of the diffusing substance. The possibility of applying these models to the problems of transfer through vitreous inorganic and polymeric membranes has been discussed.
The bibliography contains 110 references.

CONTENTS

I. Introduction 520
II. The influence of the interactions between the particles on the rates of the elementary processes 521
III. Equations for the transfer process 524
IV. Equations for the change in the state of the membrane 525
V. Vitreous inorganic and polymeric membranes 526

I. INTRODUCTION

Inorganic membranes represent a wide range of inorganic compounds which can be used to separate mixtures of substances. The materials used for inorganic membranes include metals, alloys, metal oxides, silicate glasses, ionic crystals, and zeolites.

The problem of the transfer of hydrogen in metals and alloys is of the greatest scientific and technical importance. It is related to the solution of a large number of problems: the purification and enrichment of gas mixtures;[1-3] membrane catalysis, used in hydrogenation and dehydrogenation processes to obtain highly pure substances, monomers for synthetic materials, intermediates for the production of vitamins, drugs, and dyes;[4,5] hydrogen power engineering,[3,6] etc. The higher permeability of silver catalysts[4,5] and catalysts based on simple and complex oxides[7-10] towards oxygen is also used in membrane catalysis to increase the selectivity of redox processes. Silicate glasses and ionic crystals are widely used to obtain membranes for ion-selective electrodes, used in analysis.[11] The high permeability of glasses towards inert gases, particularly helium,[1,2] is a prerequisite for the technical application of the glasses in gas-separation processes. Molecular sieves based on natural and synthetic zeolites[12,13] have widely different permeabilities for different substances, so that they can be used in gas separation and membrane catalysis.

Inorganic membranes have a high selectivity and increased mechanical strength and thermal stability compared with membranes based on organic polymers, and this makes them irreplaceable at high temperatures.

A basis for the description of the processes of mass transfer through membranes[14-40] is provided by the following scheme (Fig.1). The stream of the substance is supplied to the membrane surface *a*, where it is adsorbed and dissolves in the region next to the surface. The substance diffusing then passes through the volume phase of the membrane and leaves it through the surface *b*. In Fig.1, *k* denotes the number of the crystallographic layers perpendicular to the direction of the flow of the substance; the thickness of these layers is approximately equal to the diameter of the particles of the substance diffusing. κ_a and κ_b denote the thickness of the membrane surface regions, whose properties may differ considerably from one another and from those of the bulk phase. In the general case, $\kappa_a \neq \kappa_b$; in most of the works cited, it is assumed that $\kappa_a = \kappa_b = 1$.

Models of the processes involved in the solution and transfer of substances in solids are based on diffusion equations, supplemented by appropriate boundary conditions. Various questions related to the derivation of expressions for the diffusion coefficient and the search for boundary conditions based on a discrete scheme of randomly moving particles,[22,36] the role of saturation of the volume and the surface by the particles of the substance diffusing,[14-17,19,21,23,24,26,29] allowance for the non-equilibrium character of the processes in the surface regions and in the bulk of the membrane,[18,20,25,27,28,30,32,34,35,37,38,40] and the influence of the asymmetry of the membrane and the contribution of surface and volume defects[31,33,35,39] have been examined in detail.

In the one-dimensional model, the values of the local concentrations of the particles are related to a particular layer *k*; these values are the average values in the volume of the given layer. In macro-non-uniform systems, this scheme may be over-simplified. In layer and composite membranes, it is necessary to take more detailed account of the distribution of the non-uniform regions of the membrane within each layer,[41,42] and this makes it necessary to use two-dimensional instead of one-dimensional models of the transfer process.

All the models used at present are based on the description of the rates of the elementary processes of adsorption–desorption and migration of the particles from the law of mass action,[43] which assumes that all the particles are distributed randomly and that each behaves independently of the others. This assumption is justified only when the concentration of the particles is low. Another important assumption made in most models of mass transfer is the assumption (explicit or implicit) that the membrane is inert and that its role reduces to the determination of the sequence and inter-relationship of the absorption centres (these are usually interstices) involved in the transfer of the particles.

In many situations, these assumptions do not reflect the real properties of the systems and the conditions under which the transfer processes take place, since they are made without allowance for complex cooperative effects. Two groups of cooperative effects can be distinguished. The first is associated with a high density of sorbed particles. Most of the sorbed particles form a relatively strong bond with the solid, leading to their adsorption on the surface and absorption in the volume. The total quantity of sorbed molecules may be comparable with the number of adsorption and absorption centres. In this situation, the average distance between the sorbed particles is comparable with their dimensions, and at these inter-particle distances, appreciable interactions are possible (the nature of these interactions will not be made more specific here[44–47]). This leads to the appearance of different phase states of the sorbed particles, in particular their separation into layers and (or) ordering.[47–50] The phase state of the sorbed particles depends on their local concentration and on the temperature of the system.

The second group of cooperative phenomena is associated with the interaction of the sorbed particle with the atoms of the solid, leading to a change in the distribution of the components of the membrane in the bulk and in the surface regions, compared with their distribution in the absence of the molecules of the gas phase. In many cases, hydrogen and oxygen form chemical compounds with metal atoms, leading to a change in the properties of the membranes (a whole series of solid solutions with variable composition may be formed). This is reflected in the appearance of hysteresis on the sorption–desorption graph, an increase in the volume of the metal when the stream of gas passes through it, cracking of the metal, etc.[51,52] The energy stresses arising when hydrogen is dissolved have been estimated.[53] Similar cation redistribution phenomena are observed in solid electrolytes[54,55] and zeolites.[12] The nature of the change in the state of the solid depends on the intensity of the flux of the diffusing substance.

II. THE INFLUENCE OF INTERACTIONS BETWEEN THE PARTICLES ON THE RATES OF THE ELEMENTARY PROCESSES

The cooperative character of the transfer processes influences primarily the rates of the elementary processes. The transfer of a substance through a membrane consists of at least two stages: adsorption–desorption and migration. If the membrane is a catalyst, stages involving the adsorption and desorption of another reagent and the stage of chemical transformation also take place on one of its sides. The interactions between the particles influence the rates of each stage, and hence the rate of the overall process.

The description of the rates of the elementary processes will be based on the fundamental postulates of the theory of absolute reaction rates,[56] the initial version of which is applicable to ideal systems, that is to systems of non-interacting particles.

It is not possible to take formal account of the non-ideal nature of the system[56–58] using the activity coefficients of the reagents and the activated complexes, since the calculation of the activities in turn requires model representations of the interactions between the particles and of the structure of the condensed phase. When allowance is made for the interaction of neighbouring particles,[59] the generalisation of the expression derived from the theory of absolute reaction rates leads to a change in the concentration dependence of the rates of the elementary processes. The reason for this can be illustrated for the bimolecular reaction $iZ + jZ$, where i, j = A or v, AZ is an adsorption centre occupied by a particle A, and vZ is an unoccupied centre. With this notation, the stage involving the adsorption of an A_2 molecule is written as $A_2 + 2vZ \rightleftarrows 2AZ$, and the stage involving the migration of the particles is written as $AZ_k + vZ_q \rightleftarrows vZ_k + AZ_q$, where the indices k and q correspond to the numbering of neighbouring centres in the volume or on the surface. A uniform lattice in which each site has z neighbours can be

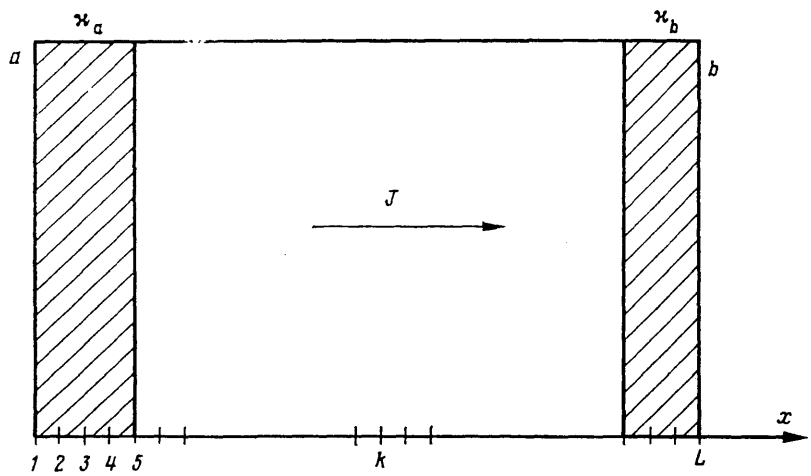


Figure 1. Diagram of a membrane; k is the layer number, κ_l is the thickness of the surface region l, $l = a, b$.

considered. For planar lattices, the sites correspond to adsorption centres, and for these, $z = 3$, 4, or 6; in volume lattices, the sites correspond to absorption centres, and for these, $z = 4$, 6, 8, or 12.

When there is no interaction between the particles, the rate of the reaction $iZ + jZ$ is expressed as $V_{ij} = k_{ij}\theta_i\theta_j$, where k_{ij} is the reaction rate constant, and $\theta_i(\theta_j)$ the concentration of the component $i(j)$ (its mole fraction), which characterises the probability that any site of the lattice is occupied by a particle of type $i(j)$. (Subsequently, quantities relating to different regions of the lattice: on the surface, in the bulk, or in a specific layer of the membrane, will be distinguished.) The normalisation condition is

$$\sum_{i=1}^{s} \theta_i = 1,$$

where s is the number of components of the system, including the unoccupied sites v. Usually,

$$k_{ij} = \hat{k}_{ij}\exp(-\beta E_{ij}),$$

where E_{ij} is the activation energy of the reaction, $\beta = (kT)^{-1}$, and k_{ij} the pre-exponential factor in the expression for the rate constant. If $i = j = A$, then k_{AA} is the rate constant of the desorption; if $i = A, j = v$ (or vice versa), then k_{Av} is the rate constant of the migration; if $i = j = v$, then $k_{vv} = k_{vv}p_{A_2}\exp(-\beta E_{vv})$ is the effective rate constant of the adsorption, where the partial pressure of the molecules of the gas phase p_{A_2} has been included to ensure uniform-ity of the form of the expression for the rate V_{ij}.

The influence of the interaction of neighbouring particles is revealed primarily by the fact that the height of the activation barrier of the elementary reaction changes with change in the local composition. $E_{ij}(n\sigma)$ denotes the energy of the interaction of the reagents ij with their neighbours in the ground state, and $E^*_{ij}(n\sigma)$ the energy of the interaction of the activated complex with its neighbours in the transition state. The configuration of neighbouring particles is given by the indices n and $\sigma(n)$, where n defines the number of neighbouring particles A in the sites of the first coordination sphere around the pair of reagents ij, and $\sigma(n)$ defines the way in which they are arranged for a fixed value of n (Fig.2). The difference $E^*_{ij}(n\sigma) - E_{ij}(n\sigma)$ gives the change in the height of the activation barrier for a given local configuration $n\sigma$. For a fixed position of all neighbouring particles, the rate of the elementary process at the two central sites is written as follows:

$$V_{ij}(n\sigma) = k_{ij}\theta_{ij}(n\sigma)F_{ij}(n\sigma),\quad F_{ij}(n\sigma) = \exp\beta[E^*_{ij}(n\sigma) - E_{ij}(n\sigma)]. \qquad (1)$$

where $\theta_{ij}(n\sigma)$ is the probability of existence of the configuration $n\sigma$ round the central particles ij. This quantity is the probability of a complex event, and to determine the reaction rate it must be expressed in terms of θ_i.

The expression for the rate V_{ij} of the reaction being considered, related to the entire surface, is obtained by averaging the expression (1). If $\alpha_{ij}(n\sigma)$ denotes the statistical weight of the configuration $n\sigma$, then

$$V_{ij} = k_{ij}\sum_{n}\sum_{\sigma(n)}\alpha_{ij}(n\sigma)\theta_{ij}(n\sigma)F_{ij}(n\sigma) \qquad (2)$$

where the first summation is carried out over the number of particles n, and the second is carried out over the different configurations $\sigma(n)$ for a fixed value of n. The set of configurations of particles A for a planar lattice with $z = 4$ is shown in Fig.2.

The paired interactions between nearest neighbours can be taken into account.[59] ε_{ij} denotes the magnitude of the interaction of particles i and j occupying neighbouring sites and present in the free state. Naturally, $\varepsilon_{ij} = \varepsilon_{ji}$. If one of the particles is an unoccupied

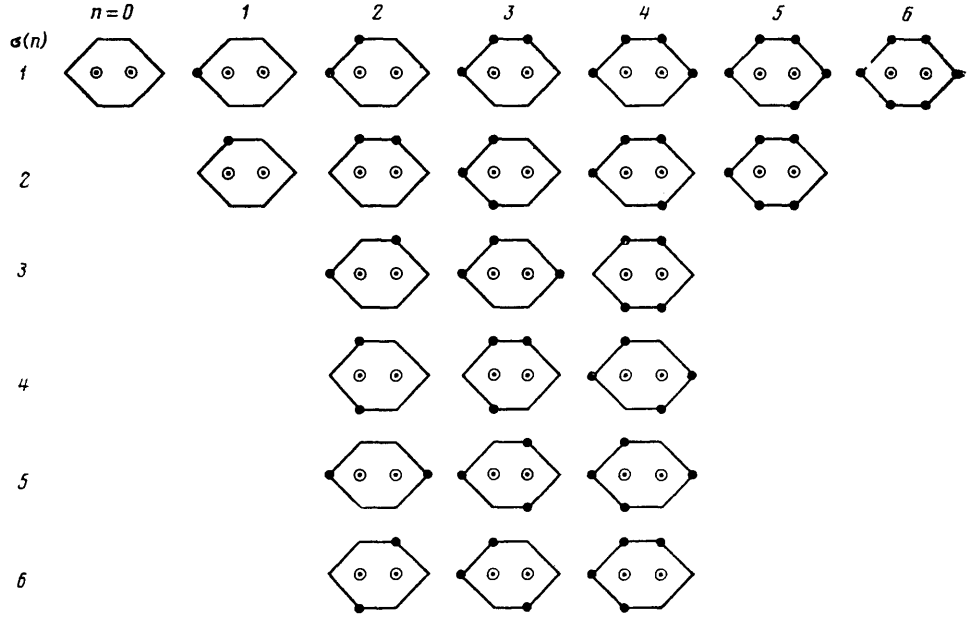


Figure 2. Configurations of particles A in the first coordination sphere round the central particles in a square lattice; the light circles represent the central particles, and the black circles the adsorbed particles A.

site, then $\varepsilon_{iv} = 0$. The formation of the activated complex involves the transfer of particles from the ground state to the activated state, corresponding to a change in the positions of the reagents relative to their neighbours. The energy of the interaction of the reagent i with a neighbouring particle j in this transition state is denoted as ε^*_{ij}. Although $\varepsilon^*_{iv} = 0$, nevertheless $\varepsilon^*_{vA} = \varepsilon^*_{AA}$, since the interaction of the activated complex with its neighbours is independent of the direction of the reaction. For paired interaction of the particles, the magnitude of $E_{ij}(n\sigma)$ is independent of the way in which the particles are arranged:

$$E_{ij}(n\sigma) = \varepsilon_{ij} + \varepsilon_{iA}n_1 + \varepsilon_{iv}(z-1-n_1) + \varepsilon_{jA}n_2 + \varepsilon_{jv}(z-1-n_2) \quad (3)$$

where n_1 and n_2 are the numbers of particles A around the particles $i(n_1)$ and $j(n_2)$, so that $n_1 + n_2 = n$. This expression has the following structure: the term ε_{ij} corresponds to the interaction of the original reagents, the next two terms correspond to the interaction of the particle i with its neighbours, and the last two terms to the interaction of the particle j with its neighbours. One of the sites closest to each central site is occupied by the other reagent, and the remaining $z - 1$ sites are occupied by neighbouring particles. For the activated complex, the interaction of its fragments "i and j" relates to the internal energy, so that in the expression for $E^*_{ij}(n\sigma)$, the first term ε_{ij} is not present, and the other terms contain ε^*_{ij} instead of ε_{ij}. This leads to the expression

$$F_{ij}(n\sigma) = \exp\beta[-\varepsilon_{ij} + n_1\delta\varepsilon_{iA} + (z-1-n_1)\delta\varepsilon_{iv} + n_2\delta\varepsilon_{jA} + (z-1-n_2)\delta\varepsilon_{jv}] \quad (4)$$

where $\delta\varepsilon_{ij} = \varepsilon^*_{ij} - \varepsilon_{ij}$.

Only one of the simplest methods of calculating the functions $\theta_{ij}(n\sigma)$ will be considered. It will be assumed that all the configurations with different $\sigma(n)$ are equally probable [for example, $\theta_{ij}(31) = \theta_{ij}(34)$]. Taking account of the distribution of the particles A in neighbouring sites round different central particles, it is then possible to write:

$$\sum_{\sigma(n)} \alpha_{ij}(n\sigma) = C^{n_1}_{z-1}C^{n_2}_{z-1},$$

where $C^{n_1}_{z-1}$ is the number of combinations of n_1 from $z - 1$. The function $\theta_{ij}(n\sigma)$ can be written as

$$\theta_{ij}(n\sigma) = \theta_{ij}t_{iA}^{n_1}t_{jA}^{n_2}t_{iv}^{z-1-n_1}t_{jv}^{z-1-n_2}$$

This form of expression indicates that the probability of a given many-particle configuration is approximated by the probabilities of simpler events, namely the probability of finding the particle i (θ_i) and the probability of finding the particles i and j in a pair of neighbouring sites (θ_{ij}): $t_{ij} = \theta_{ij}/\theta_i$, where t_{ij} is the conditional probability of finding a particle j next to a particle i; $\theta_{iA} + \theta_{iv} = \theta_i$. This is the so-called quasi-chemical approximation.[60,61] With allowance for the foregoing, including Eqn.(4), the expression (2) can be rewritten as follows:[59,64,67]

$$V_{ij} = k_{ij}\exp(-\beta\varepsilon_{ij})\sum_{n_1=0}^{z-1} C^{n_1}_{z-1}\Phi_{iA}^{n_1}\Phi_{iv}^{z-1-n_1} \times \times \sum_{n_2=0}^{z-1} C^{n_2}_{z-1}\Phi_{jA}^{n_2}\Phi_{jv}^{z-1-n_2} = k_{ij}\exp(-\beta\varepsilon_{ij})(S_iS_j)^{z-1} \quad (5)$$

where

$$S_i = \Phi_{iA} + \Phi_{iv}, \quad \Phi_{ij} = t_{ij}\exp(\beta\delta\varepsilon_{ij})$$

In the general case of an arbitrary number of components s, the functions θ_{ij} can be determined in terms of the concentrations of the particles by solving the system of equations (equilibrium distribution of the particles):[61]

$$\theta_{ii}\theta_{jj} = \theta_{ij}^2\exp[\beta(\varepsilon_{ii} + \varepsilon_{jj} - 2\varepsilon_{ij})], \quad \sum_{j=1}^{s}\theta_{ij} = \theta_i, \quad \sum_{i=1}^{s}\theta_i = 1 \quad (6)$$

The expressions for the rates of the elementary processes taking place on one and on two sites can be written in the form:[59]

$$V_i = k_i\theta_i(S_i)^z, \quad V_{ij} = k_{ij}\exp(-\beta\varepsilon_{ij})\theta_{ij}(S_iS_j)^{z-1}, \quad S_i = \sum_{j=1}^{s} t_{ij}\exp(\beta\delta\varepsilon_{ij}) \quad (7)$$

When the particles interact, the form of the expressions for the reaction rates changes as a result of the appearance of the functions S_i and as a result of the change in the probability that the reagents meet ($\theta_{ij} \neq \theta_i\theta_j$). When the reaction rates of each stage in the forward and back directions are equal, the equilibrium relationships between the concentrations of the particles are obtained with allowance for the interaction between nearest neighbours.[59] The interactions between the particles alter considerably the kinetic characteristics of the adsorption–desorption processes[62–64] They justify the empirical equations of Becker and Langmuir for the rate of desorption and of Zel'dovich and Roginskii for the rate of adsorption in chemisorption on uniform surfaces (the linear dependence of the logarithms of the rates of the processes on the degree of coverage) and the power dependence of the rate of desorption on the degree of coverage (Benham–Bart–Kwan kinetics),[65] and explain the existence of ranges corresponding to rapid and slow chemisorption.[66] The effects of correlation between particles being repelled leads to the splitting of the thermodesorption spectra on a uniform surface.[63]

Eqns.(7) can be used to estimate the self-diffusion coefficient D^*_i, characterising the transfer of a labelled component i under equilibrium conditions.[59,67,68] θ^*_{ik} denotes the fraction of the labelled component i in the layer k. The flux of the labelled particles J in the direction of the x axis is represented as the difference between the numbers of labelled particles A transferred in unit time into neighbouring vacancies from the layer k into the layer $k + 1$ and vice versa:

$$J = k_{iv}(\theta^*_{ik} - \theta^*_{i,k+1})t_{iv}(S_tS_v)^{z-1} \quad (8)$$

Comparison of this equation with the expression for Fick's first law ($J = -D^*_i d\theta^*_i/dx$) with the condition that the change in the concentration of labelled particles between neighbouring layers is small ($\theta^*_{i,k+1} = \theta^*_{ik} + ad\theta_i/dx$, where a is the lattice parameter) gives:

$$D^*_i = a^2k_{iv}t_{iv}(S_tS_v)^{z-1} \quad (9)$$

Expressions for the self-diffusion coefficient taking account of the interaction between the particles using other approximations, and for other mechanisms of migration, are obtained analogously.[69] In multi-component systems, the concept of self-diffusion coefficient is defined in different ways.[69] Nevertheless, in each specific case, it can be expressed in terms of the rates of jumping of the particles. In general, the situation is more complex than described here in terms of the traditional approach.[56,69] The complication is due to the fact that, for a number of mechanisms, there is a correlation between successive jumps of the particles, leading to the appearance of a correlation factor in Eqn.(9).[69] According to available estimates, for a binary system in the absence of interaction it varies from 1 to 0.65 for $0 \leqslant \theta \leqslant 1$.[70] This model has been used[71] to explain the anomalously low values of the activation energies of self-diffusion in the metals γ-U, β-Ti, and β-Zr.[72]

The expressions obtained for the elementary processes make it possible to construct kinetic equations describing the change in the surface concentrations of adsorbed species during surface reactions. These reactions, on the one hand, are of fundamental interest for membrane catalysis, and on the other hand define the boundary conditions for the processes of mass transfer through a membrane. The form of these equations can be examined for a model example. It will be assumed that the following three-stage process takes place: 1) $A_2 + 2Z \leftrightarrows 2AZ$, 2) $B + Z \leftrightarrows BZ$, 3) $AZ + BZ \rightarrow 2Z + C$. The first stage may represent, for example, the dissociative adsorption of hydrogen molecules in hydrogenation or dehydrogenation, or the adsorption of oxygen molecules in redox reactions. The second stage corresponds to the adsorption of the other reagent, and the third to the formation of the product C. If the given process takes place on one side of a membrane with a uniform surface, the kinetic equations have the form (in the adsorption system, three components are considered: A, B, and v):

$$\begin{gathered}\dot{\theta}_A = z[V_{vv}(1) - V_{AA}(1) - V_{AB}(3)] \\ \dot{\theta}_B = V_v(2) - V_B(2) - zV_{AB}(3) \\ \theta_A + \theta_B + \theta_v = 1\end{gathered} \tag{10}$$

The significance of the terms on the right-hand sides of Eqns.(10) can be seen from Eqns.(7); they contain the additional indices of the stage numbers ($\alpha = 1, 2, 3$), since the parameters of the interaction $\varepsilon_{ij}^{*}(\alpha)$ are different for different stages. If the reaction involves the molecules of the gas phase, the effective reaction rate constant contains as a factor the partial pressure of the substance involved in the given stage α.

If the process takes place on a catalytic membrane and the component A is transferred through it to the surface b on which the component B is adsorbed, the kinetic equations for the component A on the different surfaces have the form:

surface a:

$$\dot{\theta}_A = z[V_{vv}(1) - V_{AA}(1)] - I_A(a)$$

surface b:

$$\dot{\theta}_A = I_A(b) - zV_{AB}(3) \tag{11}$$

where the term $I_A(l)$, $l = a, b$ denotes the flux of the particles A from the surface l into the bulk of the membrane (the expression for I_A is given in the next section). The process of transfer of the component A corresponds to the stage $\alpha = 4$. The kinetic equation for the component B relates to the surface b, and its form coincides with that of expression (10).

The kinetic equations (10) and (11) are based on Eqns.(6) and (7), which are applicable when the surface mobility of the particles is high, ensuring their equilibrium distribution. This situation is apparently always realised for hydrogen atoms. For the atoms of oxygen and other moleecules, denoted B, it is possible to have situations in which the rate of their migration is comparable with the rate of the elementary reactions. The system of kinetic equations (10) and (11) must then be altered,[73,74] since Eqns.(6) are replaced by the kinetic equations for the functions θ_{ij}.

III. EQUATIONS FOR THE TRANSFER PROCESS

It is simplest to examine the characteristic features of models with restricted mobility of the particles for the case of the migration process. It will be assumed that the component A is transferred in the volume of the membrane through the interstices (vacancy mechanism). The concentration of particles in the layer k, denoted by θ_k, changes as a result of the exchange of the particles with the vacancies of neighbouring layers:[75]

$$\dot{\theta}_k = -z_{k,k-1}(V_{k,k-1}^{Av} - V_{k,k-1}^{vA}) - z_{k,k+1}(V_{k,k+1}^{Av} - V_{k,k+1}^{vA}) \tag{12}$$

where z_{kq} is the number of sites in the layer q, adjacent to a site in the layer k;

$$q = k,\ k \pm 1,\ \sum_q z_{kq} = z_k,$$

and z_k is the number of neighbouring sites for a site in the layer k. For uniform lattices, the numbers z_k and z_{kq} are constant for all the layers, whereas for non-uniform lattices these numbers are different. The quantity V_{kq}^{Av} is the rate of migration of a particle A from a site of the layer k into a vacancy of the layer q.

$$V_{kq}^{Av} = k_{Av}\theta_{kq}^{Av} \prod_{p=k+1}^{k-1} [S_{kp}^{A}(4)]^{z_{kp}-\Delta_{qp}} \prod_{p=q+1}^{q-1} [S_{qp}^{v}(4)]^{z_{qp}-\Delta_{kp}} \tag{13}$$

where Δ_{kq} is the Kronecker symbol, and the functions S_{kq}^{i} represent the generalisations of Eqns.(7) for the case of a non-uniform distribution of the particles in the lattice sites:

$$S_{kq}^{i}(\alpha) = \sum_{l=1}^{s} \theta_{kq}^{il} \exp[\beta\delta\varepsilon_{il}(\alpha)]/\theta_k^i \tag{14}$$

Eqns.(13) and (14), obtained in the quasi-chemical approximation, show that the right-hand sides of Eqns.(12) contain the unknown functions θ_{kq}^{ij}, that is the system of equations (12)–(14) is not closed. In Eqns.(12) the same migration process leads to a change in the concentration of the particles in each layer and a change in the concentration of pairs of neighbouring particles, influencing through the inter-particle interaction the height of the activation barrier of the elementary process. Thus for the system of kinetic equations (12) to be closed, it is necessary to add to it the kinetic equations for the functions θ_{kq}^{ij}. With allowance for the normalisation relationships

$$\sum_{j=1}^{s} \theta_{kq}^{il} = \theta_k^i; \quad \sum_{i=1}^{s} \theta_{kq}^{il} = \theta_q^l; \quad \sum_{i=1}^{s} \theta_i = 1 \tag{15}$$

For the binary system A–v, it is sufficient to introduce one equation for the function θ_{kq}^{AA}:

$$\dot{\theta}_{kq}^{AA} = -\sum_{h=k+1}^{k-1} (z_{kh} - \Delta_{qh})[V_{hkq}^{\overline{vA}A} - V_{hkq}^{\overline{Av}A}] - \sum_{h=q+1}^{q-1} (z_{qh} - \Delta_{kh})[V_{kqh}^{A\overline{Av}} - V_{kqh}^{A\overline{vA}}]$$

$$V_{hkq}^{\overline{vl}l} = V_{hk}^{vl}\psi_{kq}^{il}, \quad \psi_{kq}^{il} = \theta_{kq}^{il}\exp[\beta\delta\varepsilon_{il}]/(\theta_k^i S_{kq}^i) \tag{16}$$

where the first summation corresponds to the migration of a particle A from the layer k into a neighbouring site of the layer h and back again, and the second summation corresponds to the migration of another particle A from the layer q into a neighbouring site of the layer h. The terms of Eqns.(16) are expressed in terms of the rates of the elementary processes (13); the "reacting" species are indicated by a bar above the symbol. The functions ψ_{kq}^{ij} take account of the influence on the rate of change in θ_{kq}^{AA} of a neighbouring particle not taking part in the elementary process at the given moment of time.

The equations for the functions θ_{kq}^{ij} are constructed assuming that after a characteristic short time interval, only one elementary process takes place.[73–76] Finally, the system of equations (12)–(16) is closed and is solved with the specified initial conditions $\theta_k(\tau = 0)$ and $\theta_{kq}^{AA}(\tau = 0)$, $q = k, k + 1$. Equations for the θ_{11}^{ij} for restricted mobility of the reagents on the membrane surface, supplementing Eqns.(10) or (11) for the model process being considered, are given in Ref.76.

Thus restricted mobility of the particles must lead to the appearance of equations for the paired distribution functions θ_{kq}^{ij} (or for t_{kq}^{ij}). This applies to diffusion-controlled reactions,[36] ideal models of systems with a high concentration of particles[70,77] and single-layer transfer,[78] and ideal models of transfer processes with an arbitrary concentration of particles.[73-76,79]

The phase interface produces a change in the properties of the surface regions of solids. This is revealed in a change in the distance between the surface crystallographic layers and the lattice parameter in the layers, and also in structural transitions and a change in the concentration profile of the surface region.[80-83] As a result, there is a change in the properties of the absorption centres in the surface region. Study of the surface properties shows that outside the critical range, the thickness of the surface region does not exceed 5–10 layers,[82-85] but its non-uniformity may have a considerable influence on the characteristics of the membrane permeability. In the surface region, the structure of Eqns.(12)–(16) remains unchanged (the layer $k = 1$ corresponds to the surface layer of adsorbed particles), but in the terms it is necessary to replace the parameters ε_{ij}, ε_{ij}^{*}, and k_{Av} by the analogous parameters ε_{kq}^{ij}, ε_{kq}^{ij*}, and k_{kq}^{Av}, depending on the layer number. Thus $I_A(a) = V_{12}^{Av} - V_{12}^{vA}$, and analogous expressions are applicable for $I_A(b)$.

For long times ($k_{Av}\tau \gg 1$), instead of the discrete system of equations, it is possible to use the diffusion equation

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial}{\partial x}\left(D(\theta)\,\frac{\partial\theta}{\partial x}\right);\quad x = (k-\varkappa)\,a \tag{17}$$

for which the system of equations for $0 \leqslant k \leqslant \kappa$ represents the boundary condition relating the bulk value of the concentration θ to the concentration of particles in the gas phase. In the diffusion approximation, $\dot{\theta}_{\kappa-1}^{A} = 0$,[29,75] so that the equation for the layer $\kappa - 1$ can be written in the form

$$D(\theta)\,\frac{d\theta}{dx} + z_{\varkappa-1,\varkappa-2}\,(V_{\varkappa-1,\varkappa-2}^{vA} - V_{\varkappa-1,\varkappa-2}^{Av}) = 0 \tag{18}$$

The form of the other equations in the surface region depends on the relationship between k_{Av} and k_{kq}^{Av}. If $k_{kq}^{Av}\tau \ll 1$, it is necessary to use the original system of differential equations; otherwise, for all intermediate layers $\dot{\theta}_k^{A} = 0$, leading to the appearance of an algebraic relationship between $\theta_A(x = 0)$ and the pressure of the molecules in the gas phase. For $k_{kq}^{Av} \leqslant k_{Av}$, this relationship is determined by the steady-state relationships $\dot{\theta}_k^{A} = 0$, and for $k_{kq}^{Av} \gg k_{Av}$ it is determined by equilibrium relationships of type (6).[86] The change to the diffusion approximation also corresponds to the steady-state condition for the kinetic equations for the functions θ_{Av} in the volume of the solid. For a qualitative estimate of the diffusion coefficient (mass transfer) it is possible to use the condition of local equilibrium distribution of the particles.[71] In Ref.71 it was found that in the range of separation into layers, the diffusion coefficient may take negative values (condensation of the substance diffusing). A mathematical description was also obtained for experimental data[87] on the diffusion of oxygen atoms on the (110) face of tungsten. In the surface layers, the equations for θ_{kq}^{Av} either remain differential, if $k_{kq}^{Av}\tau \ll 1$, or become steady-state algebraic relationships of the form $\dot{\theta}_{kq}^{Av} = 0$, if $k_{kq}^{Av} \lesssim k_{Av}$, or into equilibrium algebraic relationships,[86] if $k_{kq}^{Av} \gg k_{Av}$.

IV. EQUATIONS FOR THE CHANGE IN THE STATE OF THE MEMBRANE

If the interaction between the atoms of the solid and the particles being transferred is sufficiently strong, it may lead to a change in the state of the membrane in the bulk. The non-equilibrium distribution of the substance diffusing along the thickness of the membrane leads to a redistribution of the atoms of the solid both along the thickness of the membrane and within each layer. If it is assumed that the particles of the substance diffusing migrate through the interstices of an alloy, and that the atoms of the alloy migrate, in accordance with the vacancy mechanism, through substitution lattice sites, then there arises the problem of describing the processes involved in the migration of particles of different kinds in different sub-lattices (immiscibility of the particles of different sub-lattices). For clarity, the treatment will be restricted to the case of a disordered alloy with a face-centred cubic (FCC) lattice, in which the dissolved particles occupy only octahedral interstices. The distances between the atoms of the alloy and between the particles of the substance diffusing in neighbouring interstices are greater than the distance between a particle and a neighbouring atom; in the general case, therefore, it is necessary to examine the problem in which account is taken of the interactions of not only nearest neighbours, but also more distant neighbours.[88-90]

The symbol γ will be used to denote the sites of the substitution sub-lattice of the alloy, and the symbol δ to denote the sites of the interstice sub-lattice. The equations for the evolution of the components of the alloy in the direction of the flux of diffusing substance will then have the form:

$$\dot{\theta}_k^{i}(\gamma) = -z_{k,k-1}\,[V_{k,k-1}^{i\nu}(\gamma\gamma) - V_{k,k-1}^{\nu i}(\gamma\gamma)] - z_{k,k+1}\,[V_{k,k+1}^{i\nu}(\gamma\gamma) - V_{k,k+1}^{\nu i}(\gamma\gamma)] \tag{19}$$

where $\theta_k^{i}(\gamma)$ is the mole fraction of the atoms i in the sites of the sub-lattice γ of the layer k. The structure of Eqns.(19) coincides with that of the equation for the transfer of the substance diffusing (12), which also remains applicable in the present case if its left-hand side contains $\theta_k^{A}(\delta)$, and its right-hand side the terms $V_{kq}^{A\nu}(\delta\delta)$. The indices in brackets indicate the sites of the sub-lattices containing the migrating atoms and particles, and also the vacancies. The terms of Eqns.(19), according to Ref.90, have the form ($\lambda = \gamma, \delta$):

$$V_{kq}^{i\nu}(\gamma\lambda) = \hat{k}_{i\nu}\theta_{kq}^{i\nu}(\lambda\lambda)\prod_{h=k+k_R}^{k-k_R}\prod_{r_h}\prod_{\sigma}[S_{kh}^{i}(\lambda\sigma\,|\,r)]^{\varkappa_{qh}(\lambda\sigma|r)} \times \prod_{h=q+k_R}^{q-k_R}\prod_{r_h}\prod_{\sigma}[S_{qh}^{\nu}(\lambda\sigma\,|\,r)]^{\varkappa_{qkh}(\lambda\sigma|r)}$$

$$\delta\varepsilon_{kh}^{ij}(\lambda\sigma\,|\,r) = \varepsilon_{kh}^{ij*}(\lambda\sigma\,|\,r) - \varepsilon_{kh}^{ij}(\lambda\sigma\,|\,r);$$

$$\varkappa_{kqh}(\lambda\sigma\,|\,r) = z_{kh}(\lambda\sigma\,|\,r) - \Delta_{qh}(\lambda\sigma) \tag{20}$$

where $z_{kq}(\lambda\sigma\,|r)$ is the number of sites of the sub-lattice in the layer q at a distance r from a site in the sub-lattice λ in the layer k; $\Delta_{qh}(\lambda\sigma)$ is the Kronecker symbol, equal to 1 for $q = h$ and $\lambda = \sigma$, and equal to 0 in other cases; $\theta_{kq}^{ij}(\sigma\lambda)$ is the probability of finding the particles i and j in the layers k and q in the sub-lattices λ and σ; the parameter of the interaction between i and j is denoted by $\varepsilon_{kq}^{ij}(\lambda\sigma\,|\,r)$. If the layers being considered correspond to a uniform volume, then the indices k and q can be omitted, but in the surface regions the layer number is important. In Eqn.(20), account is taken of the paired interactions with all neighbours situated within R coordination spheres, whose centres are the particles i and v (if the neighbours are situated in the layers $k \pm k_R$ and $q \pm k_R$ respectively). The quantity k_R differs from R, since the distance between neighbouring coordination spheres r and $r + 1$ does not exceed the

distance between neighbouring layers. For example, for a volume lattice with $z = 6$ with $R = 2$, the quantity $k_2 = 1$, as with $R = 1$ and $R = 3$; the distances between the particles, corresponding to $R = 1$, 2, and 3, are a, $a\sqrt{2}$, and $a\sqrt{3}$ respectively. The quantity $k_R = 2$ only for $R = 4$, when the distance between the particles is $2a$. An analogous situation is observed for any other structure.

Thus for a fixed layer number h, the product is taken over all the sites in the layer at different distances from the central particle. In the general case, these sites may belong to different sub-lattices. They must be distinguished in explicit form, since this determines the type of particles s_σ over which the summation in the functions $S^i_{kh}(\lambda\sigma \mid r)$ is carried out. The structure of the solid determines unambiguously the type σ of the sub-lattice in the layer h at a distance r from a site of type λ in the layer k. The parameter of the interaction of the activated complex, formed from a particle i in a site of the sub-lattice δ of the layer k and a neighbouring particle j situated at a distance r in a site of the sub-lattice σ in the layer h, is denoted by $\varepsilon^{ij*}_{kh}(\lambda\sigma \mid r)$; k_{iv} is the pre-exponential factor of the migration rate constant. Eqn.(20) differs from the analogous expression given in Ref.90 in that it takes account of the independent influence of each neighbouring particle j on the central particles i and v.

Eqns.(19) must be supplemented by equations for the functions $\theta^{ij}_{kh}(\lambda\sigma \mid r)$. In the general case it is necessary to examine all pairs of particles in different sub-lattices (in the interstice sub-lattices, the substitution sub-lattices, and pairs of a mixed type containing a particle in the interstice sub-lattice and an atom in the substitution sub-lattice), since they are all taken into account in the functions $S^i_{kh}(\lambda\sigma \mid r)$. These equations have the following general structure:[90]

$$\dot{\theta}^{ij}_{kq}(\lambda\sigma \mid r) = -\sum_h \varkappa_{kqh}(\lambda\sigma \mid r)\,[\overline{V^{vij}_{hkq}}(\lambda\lambda\sigma \mid r) - \overline{V^{ivj}_{hkq}}(\lambda\lambda\sigma \mid r)] - \\ -\sum_h \varkappa_{qkh}(\sigma\lambda \mid r)\,[\overline{V^{ijv}_{kqh}}(\lambda\sigma\sigma \mid r) - \overline{V^{vj}_{kqh}}(\lambda\sigma\sigma \mid r)] \qquad (21)$$

In the first summation, the sites h denote adjacent sites of the sub-lattice λ, corresponding to the first index λ in the argument of the term, $\lambda = \gamma$, δ; in the second summation, h denotes adjacent sites of the sub-lattice δ, corresponding to the last index in the argument of the term. The particles taking part in the elementary process are indicated by a bar above the symbol. The terms of Eqns.(21) are defined by the equations:

$$\overline{V^{vij}_{hkq}}(\lambda\lambda\sigma \mid r) = V^{vi}_{ik}(\lambda\lambda)\,\psi^{ij}_{kq}(\lambda\sigma \mid r)\,\psi^{ij}_{kq}(\lambda\sigma \mid r)\,\psi^{vj}_{hq}(\lambda\sigma \mid r), \\ \psi^{ij}_{kq}(\lambda\sigma \mid r) = \theta^{ij}_{kq}(\lambda\sigma \mid r)\exp[\beta\delta\varepsilon^{ij}_{kq}(\lambda\sigma \mid r)]/[\theta^i_k S^i_{kq}(\lambda\sigma \mid r)] \qquad (22)$$

The normalisation relationships have the form:

$$\sum_{j=1}^{s_\sigma} \theta^{ij}_{kq}(\lambda\sigma \mid r) = \theta^i_k(\lambda);\quad \sum_{l=1}^{s_\lambda} \theta^{ij}_{kq}(\lambda\sigma \mid r) = \theta^j_q(\sigma);\quad \sum_{i=1}^{s_\lambda} \theta^i_\alpha(\lambda) = 1 \qquad (23)$$

With allowance for these relationships, the system of equations (19)–(23) is closed, and it can be solved by specifying the initial and boundary conditions.

The above equations are readily generalised by taking account of the real characteristics of different systems in the following cases: 1) when the number of interstices does not coincide with the number of sites in the substitution lattice (for example for tetrahedral interstices in a FCC lattice); 2) when the migration of the particles of the substance diffusing takes place through interstices of different types and (or) the alloy is in an ordered state; and 3) when there is an additional displacement of the particles of different sub-lattices; in this case the atoms of the alloy move into the interstices and migrate in them, and the particles of the substance diffusing occupy vacancies in the substitution lattice.

From these equations under quasi-equilibrium conditions for individual sub-systems (sub-lattices) it is possible to obtain equations describing the distribution of the particles of the substance diffusing in different phase states (phase transformations involving ordering and separation into layers or any one of these may take place), as in Ref.55, where the analysis was carried out in the molecular field approximation. In this approximation, there are no effects of correlation of interacting particles. The question of taking account of correlation effects is central in kinetic studies. They may lead to qualitative changes in the description of the kinetic characteristics of a system.[63]

V. VITREOUS INORGANIC AND POLYMERIC MEMBRANES

The molecular models of the transfer of substances in crystalline membranes, described above, are capable of reflecting many important aspects of transfer processes in vitreous membranes. This also applies to silicate glasses[91,92] and to vitreous polymeric membranes. Since the latter are of practical importance, they will be considered in more detail. The available experimental material and an analysis of the trends in the development of transfer models indicate an analogy between the processes taking place in crystalline and vitreous solids. Thus the use of high pressures in a number of gas-separation systems[1,2,93–95] leads to a relatively extensive saturation of the membranes by the diffusing substance. In this case, the appearance of effects of mutual influence is possible. These effects may be due to either the direct interaction of the molecules or an indirect interaction through the polymeric matrix. The substance diffusing may alter the internal state of the polymeric matrix. Relaxation processes also influence the nature of the transfer.[96,97] The elementary processes in glasses, in particular the migration jumps of molecules, and the state of the glasses are inter-related.[98] This makes necessary a combined description of the evolution of the gas–matrix system.

An important role in the transfer of substances in vitreous and crystalline membranes is played by surface processes. A change in the properties of the surface alters its adsorption properties and the solubility of gases in the bulk of the membrane. The latter has a marked influence on the degree of non-equilibrium character of the mass-transfer conditions.[99–101] Thus the surface modification of polymeric membranes based on block copolymers of an arylene sulphoxide with dimethylsiloxane produces a marked change in their gas-permeability with respect to O_2, CO_2, and N_2.[102] The role of the surface in the processes involved in the transfer of ions through polymeric membranes was examined in Refs.103 and 104.

The state of a surface can be described using the multi-layer surface region scheme examined above. The main problem is the relationship between the migration processes and the evolution of the states of the glass. In Ref.98 this problem was solved by changing to the problem of the evolution of the Ising systems: the state of a given elementary volume is characterised by its "internal" energy and the energy of its interaction with a neighbouring elementary volume (the elementary volumes form a lattice in the bulk of the glass). In each elementary volume there is a set of discrete energy minima. The transitions between different energy states of the elementary volume are described by the equations of Glauber.[105,106] They are closed using the molecular field approximation.

The equations given in the previous section are also Glauber equations, but they were closed using a more accurate approximation taking account of short-range correlation effects. They can be used to obtain a description of vitreous systems if each discrete state of the elementary volume [98] is related to atoms of a definite type in the alloy. A more detailed description of the states of glasses is also possible, however, if a particular direction is distinguished in the volume and the group of possible states of the fragments of the polymer (or silicate) chain is examined relative to this direction. A change in the relative orientation of neighbouring fragments of the chains takes place either as a result of internal rotation within a given fragment or cooperatively as a result of conformational rearrangements of several fragments.[107-110] The transitions between different states are associated with the overcoming of corresponding activation barriers.

This formulation of the problem makes it possible to solve a wide range of problems associated with the transfer of substances through vitreous membranes.

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Problems related to the present state of the molecular-kinetic theory of transfer processes in solid crystalline and vitreous membranes, based on the use of information on the interactions between the particles, have been examined. The energy parameters are divided into two groups, characterising the interaction of the particles in the ground and transition states. The expressions proposed for the rates of the reactions in the forward and back directions for each stage of the process are consistent with the description of the equilibrium distribution of the particles.[59,88] This makes it possible to determine the parameters of the interaction of the particles in the ground state on the basis of independent measurements of the thermodynamic characteristics (for example the heats of adsorption and absorption, the isotherms of these processes, equilibrium diagrams, etc.).

A characteristic feature of the models taking account of the restricted mobility of the components of a solid is the existence of kinetic equations which describe the changes in the concentrations of different pairs of particles, and this makes it possible not only to characterise the evolution of local compositions but also to estimate the relative arrangement of the components, that is it makes it possible to obtain the details of the membrane structure and to describe its rearrangement. This in turn makes it possible to raise the question of the influence of the method of preparation of the membranes on their permeability.

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A Phenomenological Theory of Diffusion in Heterogeneous Media and Its Use in Describing Membrane Separation Processes

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Within the framework of a unified methodical treatment a critical analysis is given of different methods for the phenomenological description of the processes of the gas permeability of heterogeneous media: lamellar, dispersion type, containing individual inclusions, etc. The introduction of a continuous geometrical factor allows generalised expressions for the effective transport parameters to be obtained. Mathematical modelling methods are used to check the adequacy of the mathematical apparatus considered. The prospects for a directed choice of the structure of the material for controlling the efficiency and selectivity of a gas-separating membrane are investigated.
The bibliography includes 50 references.

CONTENTS

I. Introduction 530
II. Types of heterogeneous structures and the main approaches to the description of diffusion in heterogeneous media 530
III. Analytical treatment of the permeability of two-component heterogeneous materials 532
IV. Mathematical modelling of the permeability of heterogeneous media 534
V. Selection of the structure of the material as a means of controlling the efficiency and selectivity of a gas-separating membrane 536

I. INTRODUCTION

Composite materials are today being more widely used in membrane technology. A targetted search for such materials requires the development of a systematic approach to the construction of membranes which possess a given efficiency and selectivity using substances with known diffusion properties.

The aim of this review is to consider the prospects for using the steric and chemical organisation of a heterogeneous material to control the parameters of a gas-separating membrane. Consideration is given primarily to an analysis of the current phenomenological theories of diffusion in heterogeneous media and to mathematical modelling of the permeability of various types of such media. Recommendations are given for selecting the topology of the composite material which will provide the required transport properties for the membrane.

II. TYPES OF HETEROGENEOUS STRUCTURES AND THE MAIN APPROACHES TO THE DESCRIPTION OF DIFFUSION IN HETEROGENEOUS MEDIA

The methods for setting up the mathematical apparatus for diffusion in heterogeneous media are determined by the types of structure of the heterogeneous materials.[1-3]

In a "macroheterogeneous" medium which includes non-uniformities of structure comparable with the length of the diffusion wave, there is a distinction between the mechanisms of sequential diffusion (diffusion in a lamellar membrane, in which planar non-uniformities of structure are orientated perpendicular to the direction of flow[4]), parallel diffusion (diffusion along channels isolated from each other and orientated along the direction of flow[5]), dissociative diffusion (diffusion along interpenetrating networks of defects; this can be regarded as parallel diffusion along interconnected channels between which there is reversible exchange of the atoms of the diffusant[6-8]), and the mechanism by which the diffusive flow passes round individual large obstacles of a specific shape and dimensions.[2,9-12] The phenomenological theory of mass transport in media of this type is fairly well developed (see, for example, Refs.1, 15). One exception is the problem of transport in materials containing individual large inclusions, a general solution of which is at present unknown. For such systems there are also no methods for calculating the effective coefficients of permeability and diffusion.

The main class of "microheterogeneous" structures is made up of dispersion media, i.e. solids containing a dispersion of inclusions of a specific shape and size which have different thermodynamic and kinetic properties from the base material. A phenomenological theory of transport in dispersion media was proposed by Maxwell (see Ref.14) to describe the electrical conductivity of dispersions[15-18] and then adapted to the problems of thermal conductivity[19] and diffusion.[20,21] In this model a calculation is first made of the perturbations of the lines of diffusion flow caused by an individual obstacle of a given shape (its dimensions are postulated to be much smaller than the thickness of the specimen) situated in an inifinite homogeneous medium and then the sum is taken of all the perturbations caused by an ensemble of inclusions of the same shape arranged in a specimen of infinite size. In early work this treatment was used to describe diffusion in dilute dispersions but subsquently it was developed as applied to concentrated dispersions and the orderly packing of inclusions of phases of a different nature.[5,22-27] This theory was used to describe diffusion in media containing inclusions with a simple geometrical form: a sphere, plate, cylinder, ellipsoids of rotation, etc. Unfortunately it does not take into account the possibility of a discontinuity in the concentration profile at the boundary between the inclusion and the enclosing medium. The model has a great number of variants and, depending on the method used to sum the perturbations, it leads to different expressions for the effective permeability constant. Up to the present there has been no success in using this theory to describe non-steady-state diffusion.

A model for diffusion in dispersion media which was developed independently[28,29] was first proposed to describe the kinetics of adsorption by biporous sorbents and later to describe the process of sorption of vapours by filled polymers.[30] Within the scope of this theory the kinetics of non-steady-state diffusion from the surrounding medium into a specimen of a specific shape containing identical

inclusions (the shape of the specimen and the inclusions is made arbitrary but simple: a sphere, cylinder, or plate), the dimensions of which are considerably smaller than the length of the diffusion wave, are discussed. Linear and non-linear situations were analysed and expressions given for the initial statistical moments from the kinetic curve, so permitting estimates of the effective diffusion coefficients to be obtained.[31] A significant limitation of this treatment, severely restricting its range of application, is the requirement that the diffusion coefficient in the inclusion be much smaller than the diffusion coefficient in the base material of the specimen.

It would appear that a description of diffusion in a dispersion of point defects can be obtained from the models discussed above by simply reducing the size of the inclusions. However, in practice the theory of diffusion in defect media was developed quite independently by adapting the mathematical machinery which describes diffusion accompanied by a chemical reaction between the diffusant and the solid. Thus, diffusion with temporary retention of the diffusant in the defects (reversible capture in the traps) is interpreted as a reversible first-order chemical reaction,[32,33] diffusion with permanent capture as an irreversible first-order chemical reaction,[34] and diffusion with capture in defects of limited capacity (i.e. diffusion with adsorption at the defects which formally obey the Langmuir isotherm) as a second-order chemical reaction.[35,37] In earlier work dilute dispersions of defects were considered and then a conversion made to essentially heterogeneous media.[38,39] This approach has been fairly well developed so far: the appropriate equations for Fick's first and second laws have been rigorously set down, the formulae for describing non-steady-state mass transport obtained, and the expressions for the effective diffusion coefficients given. For example, the expression for the effective diffusion coefficient in a concentrated dispersion of point defects takes into account the diffusion coefficients both in the enclosing medium and at the defects and also the occurrence of different types of sorption isotherm in the inclusions and in the main component of the medium.[39]

A special class is formed by structures generated from dilute dispersions of point inclusions when the volume fraction of the latter is increased (for brevity in the present work we shall call such heterogeneous substances percolation-type structures[40,41]). The importance of such structures is due to their flexibility which allows conversion from one of the types of structure discussed above to another.

In fact, dispersion of point defects occurs at low concentrations of the inclusions. As their concentration increases the point inclusions are joined together in extended formations (clusters) and the dispersion is characterised by functions for the size and shape distribution of the clusters. In spite of the random nature of the cluster formation this type of dispersion medium obeys strictly defined statistical rules and the evolution of the system can be quantitatively described in terms of percolation theory using such concepts as the percolation threshold and the critical index.[42] At a certain value of the volume fraction a continuous cluster is generated (there is "puncturing" of the membrane accompanied by a sharp change in the transport properties of the membrane). In this case, direct transfer is impossible along any of the components of the heterogeneous structure (an analogue of a lamellar medium). When the volume fraction of the new phase is increased further reversal of the phases takes place, i.e. the old phase now forms inclusions in the new.

It is clear that, depending on the volume fraction of the inclusions, diffusion in a percolation-type medium can be described as "chemical" diffusion, diffusion with reversible capture, diffusion in a dispersion medium, dissociative diffusion, or dispersion in a lamellar medium. A unified description of the evolution of the system from a diffusion point of view requires the percolation theory to be amalgamated with the equations for non-steady-state transfer. However, this course involves serious difficulties. In its current form the percolation theory requires the complete absence of transport along one of the components of the medium and is used only to describe steady-state conditions of permeability.

To sum up this short analysis of known models for diffusion in heterogeneous media the following comments can be made.

(1) There are two main approaches to setting up the mathematical machinery. The first is based on replacing the heterogeneous medium by a homogeneous medium with the same effective diffusion properties. This replacement can be made if the characteristic size of the non-uniformities in the structure is smaller than the length of the diffusion wave. The second approach is used to describe diffusion in media containing individual large inclusions whose size clearly exceeds the length of the diffusion wave. In this case account is taken of the spatial arrangement of the components of the medium, the local values of the coefficients of solubility and diffusion in each component, the shape and size of the inclusions, and also the diffusion resistance of the phase boundary.

Unfortunately up to now these two methods of describing diffusion in heterogeneous media have been developed quite independently of each other. Moreover, even within the framework of a single approach there have arisen different variants which start from almost the same physical principles but lead to different final expressions. For example, depending on the method chosen for averaging the concentration field, the permeability constant P of a dispersion of inclusions is given by the formulae:[1,27]

$$\frac{P}{P_1}=\frac{P_2+2P_1-2\Phi_2(P_1-P_2)}{P_2+2P_1+\Phi_2(P_1-P_2)}$$

where Φ_1 and Φ_2 are the volume fractions and P_1 and P_2 the permeability constants of components 1 and 2 respectively;

$$\frac{P}{P_1}=\frac{P_2+2P_2-W-\Phi_2(2P_1-2P_2-W)}{P_2+2P_2-W+\Phi_2(P_1-P_2+W)}$$

where $W = 0.78(P_2 - P_1)^2/(2P_1 + P_2)$; or

$$P_1P^3-3P_1P_2P^2+(3P_1P_2^2+(P_2-P_1)^3\Phi_1^3)P-P_1P_2^3=0$$

$$2P^2+[P_2-2P_1-3\Phi_2(P_2-P_1)]P-P_1P_2=0$$

$$\left(\frac{P}{P_1}-1\right)=3\Phi_2\left[\frac{P_2+2P_1}{P_2-P_1}-\Phi_2+\frac{\beta(P_2-P_1)\Phi_2^{10/3}}{P_2+(4P_1/3)}+\ldots\right]^{-1}$$

where for simple cubic packing of spheres $\beta = 0.523$ [15] (in Ref.23 $\beta = 1.31$), for body-centred cubic packing of spheres $\beta = 0.129$,[23] and for face-centred cubic packing $\beta = 0.0752$.[23]

An analysis of these expressions shows that they give approximately the same results if $P_2 < P_1$ but considerably different results if $P_2 > P_1$.

With such a diversity of expressions a natural question arises: which of these formulae is most valid physically and universal? Below, by analysing the known models within the framework of a single methodological approach, we shall discuss diffusion in various types of heterogeneous media (dispersion, lamellar, containing individual inclusions, etc.) and shall show that the modified Maxwell equation generated as a result of this analysis allows almost all the known methods of describing diffusion in heterogeneous media to be unified. The adequacy of the treatment will be checked by comparison with the results of mathematical modelling of diffusion in heterogeneous media.[43]

(2) Almost all the structure types described above are represented among specific polymer systems.[44,45] For example, parallel diffusion is observed in polymers with a spherulitic structure when the membrane thickness is comparable with the diameter of the spherulites.[46] Sequential diffusion takes place in lamellar membranes obtained by compressing several films with different diffusion properties, in polymers whose surface has been modified chemically or by radiation, etc. In investigating composites based on polymers and porous specimens the distortions of the diffusion flow lines must be taken into account. The geometrical form of the non-uniformities in the structure must be allowed for in work with crystalline polymers or filled materials.[47]

Diffusion with temporary retention of the diffusant in traps occurs in glassy polymers, block-copolymers, etc. A model for dissociative diffusion will, generally speaking, always be used in describing the processes of mass transport in polymers: the presence of macro-chains necessitates taking into account diffusion along two interconnected channels (along and across the chains) which involve different values of the diffusion coefficient.

The application of the theory of diffusion in heterogeneous media to real polymeric solids often leads to inadequate results: the parameters of the shape of the inclusions calculated from diffusion data do not correspond to those measured on an electron microscope.[21] This is because definite geometrical shapes for the defects in the structure are rarely met in actual systems. Furthermore, a whole spectrum of inhomogeneities in structure is usually present in the materials. Such a situation occurs, in particular, on reversal of the phases.

These difficulties can be overcome by introducing into the modified Maxwell equation a continuous geometrical factor, the values of which are either determined experimentally or calculated by mathematical modelling methods.

(3) In membrane technology a very important aim is to develop methods for a directed choice of the spatial and chemical organisation of the membrane structure, which will ensure that the efficiency and selectivity of the membrane are high. Below we shall set out a theory of diffusion in heterogeneous media for describing the permeability to mixtures of gases and demonstrate a method for choosing a spatial structure of the membrane that is optimal from the point of view of solving problems in membrane-separation of gaseous mixtures.

III. ANALYTICAL TREATMENT OF THE PERMEABILITY OF TWO-COMPONENT HETEROGENEOUS MATERIALS

The following concepts are used in setting up a phenomenological theory of mass-transport in heterogeneous media:

the topology of the medium, i.e. the spatial arrangement of the discontinuities (layers, inclusions, dispersions of inclusions, etc.);

the diffusion properties of the initial components of the medium (the coefficients of diffusion and solubility in these components of the substances being separated);

the type of sorption isotherm of the diffusant in each of the components of the medium; and

the type of diffusion experiment, i.e. a certain set of initial and boundary conditions (in the present work we were restricted to the permeability method).

The output parameters are:

the permeability constant of the heterogeneous medium P which determines the magnitude of the steady-state flow through the membrane;

the mean concentration of the diffusant in the specimen;

the effective non-steady-state diffusion coefficient being used to estimate the time taken to reach a steady state;

the form of the concentration and kinetic dependences;

the dependence of the diffusion parameters on the density of the inclusions and their shape, the structure of the heterogeneous material (thickness and form of the membrane, size of the inclusions, etc.), the partial pressure at the entrance of the membrane, the drop in pressure at the specimen, etc.

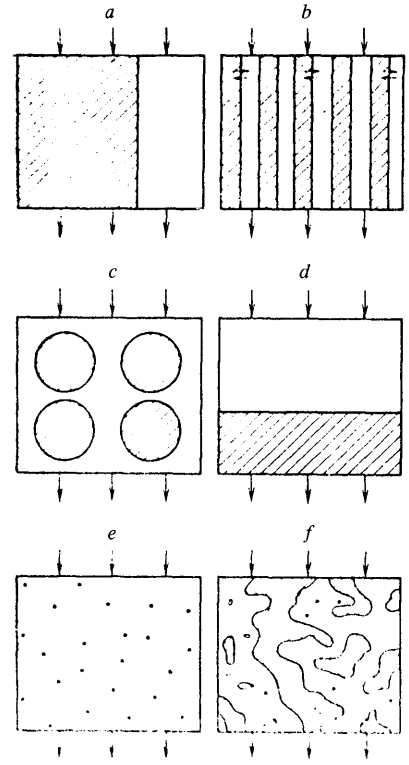


Figure 1. Main types of heterogeneous system.[2]

We are restricted to consideration of five main topological types of two-component material. In the first type of material, mass transport takes place along two channels isolated from each other, i.e. there is parallel diffusion (Fig.1*a*). In the second type of membrane there can be reversible exchange of the diffusant atoms, i.e. dissociative diffusion (Fig.1*b*). In the next type of structure the diffusion medium contains inclusions of a specific shape and size (as an example cubic packing of spheres is shown in Fig.1*c*). A lamellar medium (Fig.1*d*) gives sequential diffusion through layers of different components. The fifth type is a percolation-type structure (a dilute dispersion of point defects is shown in Fig.1*e* and a dispersion of clusters of defects in Fig.1*f*).

The process of diffusion in a heterogeneous medium is usually considered as a random walk of the diffusant particles in the energy field created by the material of the medium (the field does not

change when the diffusant particles pass through it). For a homogeneous isotropic medium the diffusion coefficient D can be represented in the form:

$$D=kd^2$$

with

$$k=k_0\cdot\exp(-\Delta G/k_BT)=\gamma f\nu_0\cdot\exp(-\Delta G/k_BT)$$

where k is the rate constant for the passage of a diffusant atom from one energy state to another, d is the length of a diffusion jump, i.e. the distance between two nearest states, γ is the number of routes by which a transition from one state to another is possible, f is a correlation factor (the fraction of successful jumps, which we shall asume to be 1), ν_0 is the number of jumps in unit time, ΔG is the energy of the transition from one diffusion state to another, k_B is the Boltzmann constant, and T the temperature.

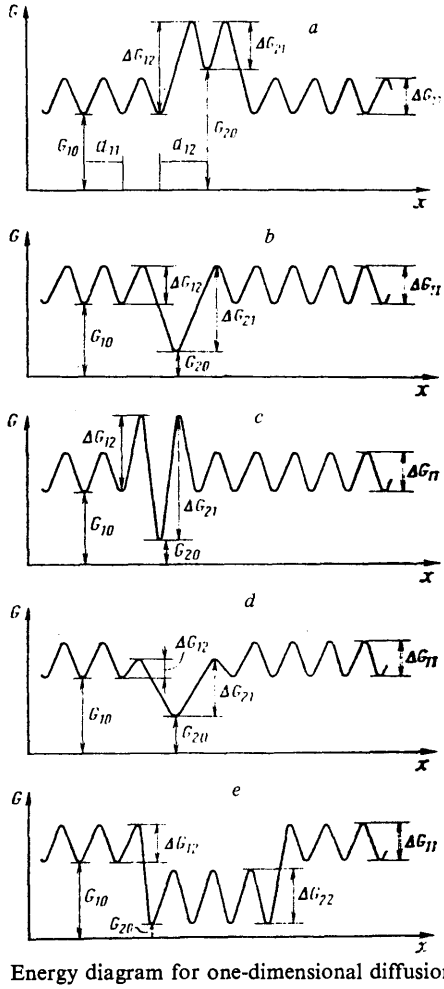


Figure 2. Energy diagram for one-dimensional diffusion (x is distance).[2]

In a two-component medium there are two types of energy state. A site in the base material of the solid will be designated by a subscript 1 and a site in a non-uniformity in the structure by a subscript 2. To describe diffusion in such a system we shall use four transition rate constants k_{11}, k_{12}, k_{21}, and k_{22} and the corresponding lengths of the diffusion jumps d_{11}, d_{12}, d_{21}, and d_{22}. All these parameters are independent of the diffusant concentration but dependent on the temperature:

$$k_{ij}=k_{ij,0}\cdot\exp(-\Delta G_{ij}/k_BT)$$

The pre-exponential factor is determined only by the nature of the diffusant.

Certain types of energy diagram for diffusion in a two-component medium are shown in Fig.2. The migration of the diffusant is determined by the positions of the two potential wells of types 1 and 2 relative to the zero level (i.e. by the energies G_{10} and G_{20}) and also by the magnitude of the energy barriers on entrance to and exit from the potential well (ΔG_{11} for a transition in the base matrix, ΔG_{12} for a transition from the base matrix to an inclusion, ΔG_{22} for diffusion in an inclusion, and ΔG_{21} for exit from an inclusion to the base material of the specimen). If the free energy is higher in state 2 than in state 1 (Fig.2*a*) it is unfavourable for the diffusant to remain in state 2 (an "anti-trap") and it tries to leave. On the other hand, a state with a lower free energy (Fig.2*b*) fills up with diffusant spontaneously (a "trap"). The transition to another phase may be hindered ($\Delta G_{12} > \Delta G_{11}$, Fig.2*c*), remain the same as on transition to an adjacent base state (Fig.2*b*), or may be facilitated (Fig.2*d*), depending on the properties of the boundary between states 1 and 2. If component 2 is an extended inclusion, transitions of type 2−2 appear on the energy diagram (Fig.2*e*).

By the local diffusion coefficient is understood the value $D_{ij} = k_{ij}d_{ij}^2$. Note that $D_{11}\equiv D_1$ and $D_{22}\equiv D_2$ (where D_1 and D_2 are the diffusion coefficients in phases 1 and 2), and that in general D_{12} is not equal to either D_{21} or D_{11}. Thus the presence of additional energy barriers at the entrance to a defect leads to a three-phase diffusion problem for a two-component heterogeneous medium.[48]

By analogy with the concepts used in describing the kinetics of chemical reactions, the value of the ratio of the rate constant for a 1−2 transition to the rate constant for a 2−1 transition is called the equilibrium constant:

$$K=k_{12}/k_{21}=D_{12}/D_{21}=\exp\{-(\Delta G_{12}-\Delta G_{21})/k_BT\}=\exp\{(G_{10}-G_{20})/k_BT\}$$

We shall now turn to a consideration of the population of the energy states of the system by the diffusant atoms. The following symbols will be introduced:

$$\Phi_1=N_1/N=V_1/V,\ \Phi_2=N_2/N=V_2/V\ (\Phi_1+\Phi_2=1)$$

are the volume fractions of components 1 and 2 respectively, where N_1 and N_2 are the numbers of states of types 1 and 2 ($N_1 + N_2 = N$), V_1 and V_2 the volumes of components 1 and 2 ($V_1 + V_2 = V$) in the composite material; the relative populations are $\theta_1 = n_1/N_1$ and $\theta_2 = n_2/N_2$, where n_1 and n_2 are the numbers of diffusant atoms occurring in states 1 and 2; the total population (solubility) of the two-component system is $\theta = n/N = (n_1 + n_2)/(N_1 + N_2)$ and the mean population is $\theta = \Phi_1\theta_1 + \Phi_2\theta_2$.

The linear sorption isotherm is described by the expression:

$$\theta(x=0)=K_\gamma p_0$$

where K_γ is the solubility constant and p_0 the partial pressure of the diffusant on entry to the membrane.

The exchange of the diffusant atoms between the two types of potential well is usually represented in the form:

$$V_1(A)+V_2(0)\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}V_1(0)+V_2(A)$$

where $V_1(a)$ and $V_2(A)$ are the diffusant atoms in potential wells of types 1 and 2 respectively and $V_1(0)$ and $V_2(0)$ are vacant sites. If each of the components of the medium is characterised by a linear sorption isotherm then the equilibrium solubility of the diffusant in the first component will be θ_{10} and in the second θ_{20}. Linearity of the sorption isotherm implies that the concentration of free sites in the matrix of the heterogeneous material is sufficiently large, i.e. the relative population is less than 1. At equilibrium:

$$n_2N_1/n_1N_2=k_{12}/k_{21}=K;\ \theta_2=K\theta_1$$

i.e. the equilibrium constant is the ratio of the local solubilities, $K = \theta_2/\theta_1$. Taking into account that the relative population of the first (main) component is not altered by the presence in the material of the second component, the total population is given by the expression

$$\bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2)$$

where θ_{10} is the population of an "ideal" material containing no non-uniformities.

There are various methods for determining experimentally the solubility of the diffusant in the solid: measurement of the mass of the specimen in a steady state of permeability, determination of the amount of diffusant in the specimen after a steady state has been reached, or by dividing the steady-state flow of the diffusant through the membrane by the diffusion coefficient determined from the time lag. In a homogeneous material all these methods give the same result and the solubility measured by the permeability method is equal to half the value determined from the equilibrium sorption. For a heterogeneous medium, on the other hand, such conformity is not observed although the relationship $\theta_2 = K\theta_1$ is always valid.

Let us turn to a consideration of the value of the permeability, i.e. the constant of proportionality between the steady-state flow of the diffusant through the membrane and the difference in the partial pressures on entry to and exit from the membrane. The symbols $\chi_2 = P_2/P_1$ and $\chi = P/P_1$ are used. The known expressions for diffusion in heterogeneous media can now be reduced to a common form of notation.

For dissociative diffusion and its special case of parallel diffusion:

$$\chi=\Phi_1+\chi_2\Phi_2;\ \ \bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2) \qquad (1)$$

For a dispersion of inclusions of identical shape and size (modified Maxwell formula):

$$\chi=(\Phi_1+a\chi_2\Phi_2)/(\Phi_1+a\Phi_2);\ \ \bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2) \qquad (2)$$

where

$$a=a_0/(a_0-1+\chi_2),$$

a_0 being a geometrical factor depending only on the shape of the inclusion. For some simple forms of inclusion this can be calculated analytically: e.g. $a_0 = 3$ for inclusions with a spherical shape and 2 for inclusions in the form of a cylinder with its axis perpendicular to the diffusion flow, etc. Eqn.(2) is valid for dilute suspensions ($\Phi_2 < 0.3$); on changing to closest packing of the inclusions additional terms must be introduced into formula (2).[1] On the whole, Eqn.(2) is satisfied as long as the inclusions retain a definite shape and continuous diffusion flows along one of the components of the heterogeneous medium are possible. It is important to stress that when there is reversal of the phases (i.e. when the matrix and the inclusion change roles) "hysteresis" of the permeability may occur.

For a lamellar material the mean concentration of the diffusant (solubility) in the membrane for a steady state of permeability is given by the expression:[4]

$$\bar{\theta}=\theta_{10}(\chi_2\Phi_1^2+2\Phi_1\Phi_2+K\Phi_2^2)/(\chi_2\Phi_1+\Phi_2)$$

and the permeability is equal to:

$$\chi=(\Phi_1+\Phi_2/\chi_2)^{-1} \qquad (3)$$

The common form of notation for the permeability of the main types of structure which is used in the present work shows clearly the general character of the modified Maxwell formula (2), from which the other diffusion models arise as special cases when an appropriate choice of the geometrical form parameter a_0 ($a_0 \geqslant 1$) is made. The limiting cases are parallel diffusion ($a_0 = \infty$) and sequential diffusion ($a_0 = 1$). This approach allows us to extend the application of the Maxwell formula derived for the case of inclusions of a simple form (discrete integral values of a_0) to cases where the inclusions have an arbitrary structure (continuous fractional values of a_0). Numerical modelling methods can be used to find the values of a_0 for inclusions with the "exotic" shape of rectangular blocks, crosses, etc., for a lamellar medium with a variable boundary, and also to study the evolution of a_0 during reversal of the phases, which results from formation of the nuclei, growth of the nuclei of a new phase, nucleation and growth of the nuclei, etc. The value of a_0 is a measure of the distortions of the flow lines, i.e. the lines along which the product of the diffusion coefficient and the gradient of the diffusant concentration remains constant: for a given χ_2 the smaller is a_0 the greater is the distortion.

In the analysis of the permeability of a dilute dispersion of point inclusions there are considerable difficulties due to the disappearance of diffusion along the second component of the medium at small values of Φ_2. In such structures the transport properties of the material are determined mainly by the characteristics of the intercomponent boundaries. In accordance with a statistical treatment,[38] we may write, using our symbols:

$$\chi=\Phi_1^2+\frac{D_{12}+KD_{21}}{D_{11}}\Phi_1\Phi_2+\chi_2\Phi_2^2$$

Using the relation $D_{12} = KD_{21}$, we obtain:

$$\chi=\Phi_1^2+2\frac{D_{12}}{D_{11}}\Phi_1\Phi_2+\chi_2\Phi_2^2 \qquad (4)$$

$$\bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2)$$

The expressions obtained are valid for any values of Φ_2, i.e. they are suitable for describing the permeability of a dispersion of point inclusions during the complete reversal of the phases taking place by a "percolation" process.

IV. MATHEMATICAL MODELLING OF THE PERMEABILITY OF HETEROGENEOUS MEDIA

The analytical approaches to the description of diffusion in heterogeneous media which were discussed previously are valid only with various kinds of assumptions and have a limited use. Numerical methods of mathematical modelling[43] must therefore be used to solve such problems of the permeability of heterogeneous media as transport in a composite containing a concentrated dispersion of inclusions or in a medium containing irregularly shaped inclusions, when there is a complex distribution of non-uniformities through the thickness of the specimen, when there are specific energy barriers at the entry to the inclusion, etc.

In that work[43] modelling was carried out for diffusion in systems with linear sorption isotherms on the basis of the statistical treatment described above. The whole of the heterogeneous material was divided by a rectangular grid into separate cells corresponding to different diffusion states; a matrix of the energy transitions ΔG_{ij} was then set up and from it the rate constants for exchange between diffusion states of different types (k_{ij}) were calculated. After the initial and boundary conditions had been assigned the resultant system of linear differential equations was solved by a Monte Carlo method with a constant time interval.

The program[43] was intended for modelling of mass transport in a two-dimensional heterogeneous medium with an arbitrary topology of inclusions in various diffusion experiments using permeability, sorption, and desorption methods, the method of concentration waves, local diffusion probing, etc. In the course of the calculation the distribution of the concentration of the diffusant in the heterogeneous medium and the total and local flows across the outer boundaries of the specimen are indicated and the total population of the specimen by the diffusant (the solubility) is found. The program also enables a treatment of the kinetic functions to be carried out with the aim of determining the non-steady-state effective diffusion coefficient. For a "percolation" type of medium the program enables a cluster analysis of the inclusions to be carried out, the open, continuous, and closed porosities to be determined, and the mean size of the inclusions to be found.[43] A test of the program, performed for a homogeneous medium, showed a high accuracy ($\sim$0.1%) for the calculation of all the output parameters and also that the postulated functions $k_{ij} = f(\Delta G_{ij})$ are satisfied.

Modelling of diffusion in heterogeneous media was carried out for an extensive set of K, χ_2, and Φ_2 parameters for all the structures discussed above. In the first stage, situations for which analytical formulae are known were investigated and in the second, situations for which there is no phenomenological theory of diffusion.

A test of known published models showed that there is a rigorous mathematical description only for cases of parallel and dissociative diffusion and also for diffusion in a lamellar medium. When extended inclusions of a specific shape and size are present an analytical description is possible for certain simple forms (sphere, cylinder, spheroid), for which the "experimental" values of a_0 agree with the theoretical values and for $\Phi_2 \leqslant 0.3$. As Φ_2 increases the description of the process by the analytical formula becomes worse, with χ approaching χ_2 more rapidly than the theory predicts. We have obtained confirmation [34] of the occurrence of diffusion hysteresis, whereby the permeability of heterogeneous materials of identical composition depends on their method of preparation and in particular on whether a dispersion of component 2 in component 1 was prepared or vice versa. Confirmation was also obtained of the assumption that the geometrical parameter a_0 depends not only on the ratio of the width of the inclusion to its length but also on the "distorting power" of the particular form of inclusion as regards the diffusion flow lines. In particular, the modelling method gave the value $a_0 = 1.55 \pm 0.15$ for an infinite block with a square cross-section placed perpendicular to the direction of flow (the a_0 value for such a geometry cannot be calculated analytically). This value is smaller than the value $a_0 = 2$ for a cylinder because a block with a square cross-section distorts the diffusion flow lines considerably more severely.

It is important to stress that the effect of the geometry of the inclusions on the permeability depends considerably on the energy parameters of the components of the heterogeneous structure. A typical dependence of χ on K and D_2/D_1 is shown in Fig.3; the example shown is of the permeability of a dispersion medium with inclusions in the form of a cylinder, for which $a_0 = 2$ and $\Phi_2 = 0.1$. Thus, when $\chi_2 = 1$ (which does not imply at all that the diffusion properties of the components are identical, since for linear isotherms $\chi_2 = KD_2/D_1$) the permeability is independent of K and D_2/D_1. When $\chi_2 = 0$ (the case of impermeable obstacles) the permeability of the heterogeneous medium depends on both its composition and the geometry:

$$\chi = \Phi_1 \frac{a_0 - 1}{a_0 - \Phi_1} \qquad (5)$$

If, however, the inclusion is highly permeable (a pore, $\chi \to \infty$), the permeability of the heterogeneous medium increases more slowly in the general case, reaching the limiting value $\chi = 1 + a_0\Phi_2/\Phi_1$.

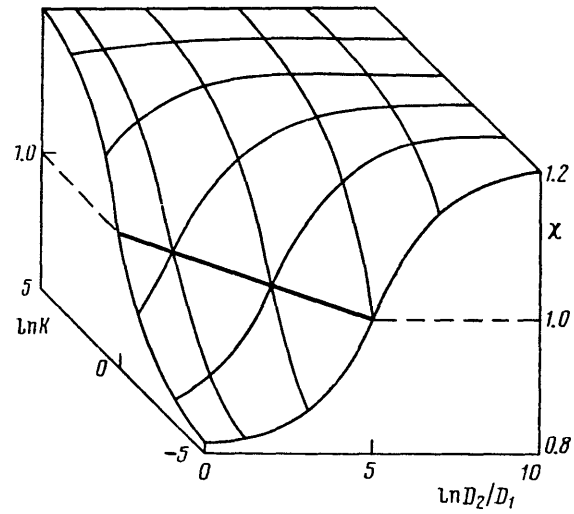


Figure 3. Dependence of the permeability on the transport parameters of a composite[2] (a lattice of cylinders, $a_0 = 2$, $\Phi_2 = 0.1$).

In the modelling of the permeability of a dispersion of point inclusions, the phenomenological model gives only a semiquantitative description. The divergence from theory reaches 20–30% but the theoretical and "experimental" functions $\chi(\Phi_2)$ change in a similar way. The theory is qualitatively correct in prediciting the occurrence of extrema in the function $P(\Phi_2)$ and also their positions, to within $\sim$10%. An attempt was made to improve the accuracy of the numerical calculation by changing the coordination number of the diffusion state from 4 to 8. The discrepancy between the theoretical and "experimental" results was then reached. We assume, although it was not stated when the phenomenological model was set up,[38] that in the statistical summation of the four types of flow it is tacitly understood that the coordination number is equal to infinity. A detailed analysis of this matter showed that, even with high values of the coordination number, complete agreement between the theoretical conclusions and the results of the mathematical experiment cannot be obtained. Thus mathematical modelling of the permeability of heterogeneous media of the "percolation" type by numerical

methods gives more reliable results because in the anlaytical treatments no account is taken of the distortion of the lines of diffusion flow around the point inclusions and their clusters.

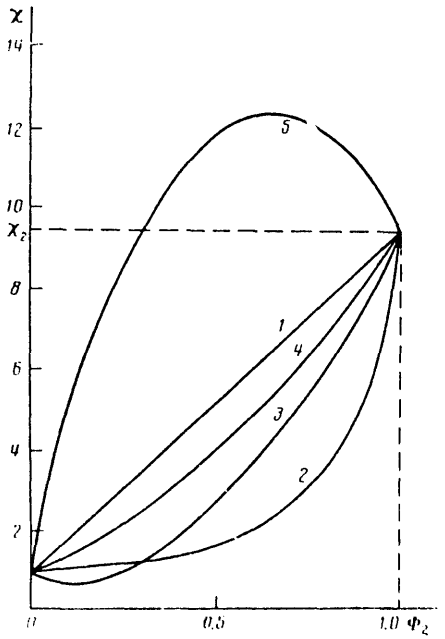


Figure 4. The permeability of percolation-type structures: *1*) parallel diffusion; *2*) a lamellar medium; *3*–*5*) percolation structures for which $D_{12} \to 0$ (*3*), $D_{11} < D_{12} < D_{22}$ (*4*), or $D_{12} \gg D_{11}$ and $D_{12} \gg D_{22}$ (*5*) (from data in Ref.43).

The dependence of the permeability on the volume fraction of the second component is shown for various types of structure in Fig.4. For almost all the structures the $\chi(\Phi_2)$ curves lie between the two limiting cases: dissociative or parallel diffusion (the straight line *1*) and diffusion in a lamellar medium (curve *2*). Exceptions are provided by dispersion structures of the "percolation" type (Fig.1*f*). As follows from Eqn.(4), the dependence of χ on the local transport parameters envisages an effect of the intercomponent layers on the transport (it has already been mentioned that in this case a situation arises which requires the solution of a "three-phase" diffusion problem for a two-component medium). Depending on the conditions at the boundary between the components, the $\chi(\Phi_2)$ curve may pass below the straight line for the limiting case $a_0 = 1$, corresponding to a low permeability of the intercomponent layer ($D_{12} \to 0$, curve *3*), with a possible minimum on the curve; or it may be completely within the permissible region (the permeability of the intercomponent layer lies between the corresponding values for the components of the medium, curve *4*) or it may be situated above the limiting straight line for $a_0 = \infty$. The last situation arises when the permeability is high at the boundary (i.e. when $D_{12} \gg D_{11}$ and $D_{12} \gg D_{22}$, curve *5*), a maximum on the $\chi(\Phi_2)$ curve being possible.

In addition to the steady-state values of the flows, permeability kinetic curves have been obtained by numerical methods[43] and the effective diffusion coefficients calculated.[49] Without discussing these results in detail we note that in a number of cases the theory predicts the possibility that substantial errors will arise in the experimental determination of the steady-state flow of the diffusant through the membrane and hence of the permeability constant. This is because a "pseudo-steady-state" of permeability may be reached for certain values of the local transport parameters; at diffusion times 2–3 times greater than the delay time an almost constant flow through the membrane (significantly smaller than the steady-state flow) is established and this may be erroneously regarded as a true steady state, although times 20–30 times longer are required to achieve the latter.

The total population (solubility) in all the types of structure considered agrees with the values predicted theoretically.

V. SELECTION OF THE STRUCTURE OF THE MATERIAL AS A MEANS OF CONTROLLING THE EFFICIENCY AND SELECTIVITY OF A GAS-SEPARATING MEMBRANE

We have so far discussed the permeability of membranes with respect to any one gas. We shall now turn to the problem of the membrane separation of a mixture of gases and assess the prospects for a directed choice of the structure of the heterogeneous medium in order to achieve the optimum efficiency and selectivity for the membrane.

Suppose that a mixture of two gases is supplied to the input side of a membrane and the process of transport of each of them through the membrane is characterised by its own set of parameters D, K, χ, and θ. These parameters are dependent on the composition and topology of the membrane but independent of the composition of the gaseous mixture. We shall take as the selectivity factor the relationship:

$$\alpha = \alpha_i \chi'/\chi'' \qquad (6)$$

where χ' and χ'' are the permeabilities of the first (object) and second gases respectively and α_i are the selectivity factors of the initial components, $\alpha = P_i'/P_i''$.

The effectiveness of operation of a gas-separating system is characterised by two parameters: the efficiency (i.e. the permeability for the object component, χ'), which determines the amount of product obtained, and the selectivity, which determines its purity. Optimisation of membrane separation is a complex problem because it is far from always possible to obtain high efficiency and a high product purity simultaneously. As is known, membrane separation can be used either to purify the flow passing through the membrane or to concentrate the object product over the membrane. The requirements for selecting χ'' and α are of course different in these cases. If the object product is the gas passing through the membrane, high values of χ' and α are chosen but in the reverse case low values of χ' and α are required.

The effects of the local transport parameters of the heterogeneous medium on the flow of the object component χ' and on the selectivity factor α are different: a decrease in D_2'/D_1' and K' leads to a reduction in χ' and α, but a decrease in D_2''/D_1'' and K'' increases α while leaving χ' unchanged. Since the change in χ' and α in heterogeneous structures of different types takes place differently, then, depending on whether the membrane works by purification or concentration, these parameters will have the optimum values for quite different spatial organisations of the material. It follows from Eqn.(6) that α is a function of six parameters (if the topological factor a_0 is taken as one of them). We shall therefore restrict ourselves to a few examples.

The first two examples are taken from Ref.50 in which measurements were made of the gas permeability of PVTMS (component 1) – PDMS (component 2) block copolymers of various compositions (PVTMS represents polyvinyltrimethylsilane and PDMS polydimethylsilane). We shall discuss Kr–Xe and H_2–Xe gas mixtures, the transport parameters of which are given in the Table (the problem of separating such gas mixtures arises in the AES gas purification system). The Table also shows the experimental values[50] of the steady-state flows and the selectivity factors together with those calculated by us for different structures. For a Kr–Xe mixture the experimental selectivity factor (α = 0.56) is close to the value calculated (0.61) for the parallel (or dissociative) diffusion mechanism (see Table, gas mixture No.1). However, there is a considerable discrepancy between the experimental and calculated values of χ' (2.04 and 10.4 respectively). This may be explained by extra resistance to transport at the boundaries between the components of the block copolymer. In this case the membrane used in the experiment is close to the optimum from the point of view of concentrating the Kr. In using a membrane for Xe purification its efficiency can be increased (by a factor of 5) if a structure which ensures a dissociative or parallel diffusion mechanism is created.

For an H_2–Xe mixture (Table, mixture No.2) the theoretical value of the efficiency with respect to the object material (H_2) is slightly dependent on the structure of the membrane and is close to the experimental value (evidently for hydrogen, resistance to diffusion at the boundary between the components does not play a significant role). However, the theoretical analysis shows that the membrane structure used in the experiment was not the optimum as regards selectivity; in this case a lamellar membrane should be used.

The possible occurrence of extremal relationships between α and the structure are demonstrated on the model example (Table, mixture No.3). Here, to obtain the optimum ratio between the flow and the selectivity a structure having a dispersion of cylinders (filaments elongated perpendicular to the flow) must be created. If, however, it is required to concentrate gas 1 over the membrane and to pass gas 2 through it, then it is better to arrange for sequential diffusion (i.e. to prepare a membrane in the form of layers orientated perpendicular to the flow).

The effect of the structure on the gas-separation parameters χ' and α is conveniently studied using the topology–property diagrams which we have proposed. To construct such diagrams (Fig.5) the reciprocal of the geometrical factor a_0 is plotted along the abscissa (the value of $1/a_0$ varies from 0, corresponding to no perturbation of the flow lines, to 1, corresponding to a severe perturbation) and χ' and α as the ordinate.

Effect of topology and local transport parameters on the permeability (χ') and selectivity (α) of a heterogeneous membrane.*

Mixture no.	Gas	D_2/D_1	K	α_1	Parameter	Calculated for different types of structures**				Experimental (Ref.50)
						I	II	III	IV	
1	Kr	47.9	0.67	1.5	χ'	10.4	1.79	1.41	3.81	2.04
	Xe	160.4	0.52		χ''	25.6	1.82	1.41	8.37	—
					α	0.61	1.46	1.49	0.68	0.56
2	H_2	2.10	1.19	11.0	χ'	1.45	1.30	1.22	1.13	1.4
	Xe	160.4	0.52		χ''	25.62	1.82	1.41	8.37	—
					α	0.62	7.8	9.4	1.5	2.7
3	1	0.1	1.0	7.0	χ'	0.73	0.61	0.27	0.54	—
	2	10.0	5.0		χ''	15.71	1.81	1.42	5.40	—
					α	0.32	2.34	1.33	0.70	—

*The parameters χ', χ'', and α for the gas mixtures nos.1 and 2 were calculated using published experimental data;[50] gas mixture no.3 is a model.

**Φ_2 = 0.3; I) parallel diffusion; II) a dispersion of cylinders; III) a lamellar medium; IV) a dispersion of point inclusions.

These diagrams first of all enable the geometrical factor a_0 to be estimated from gas permeability data. a_0 can be determined experimentally by measuring either the efficiency of the membrane or the selectivity factor. Agreement between the values of a_0 found by different methods indicates the absence of resistance at the boundary between the components. The discrepancy between the values of a_0 obtained from χ' and α (in Fig.5 the range of uncertainty for a_0 is shaded) is large for the Kr–Xe mixture (Fig.5*a*), far larger than the corresponding range for the H_2–Xe mixture (Fig.5*b*).

Such diagrams can thus be used for diffusion-structure analysis, i.e. to determine the topological characteristics of a membrane used in a separation process. On the other hand, they can be used to

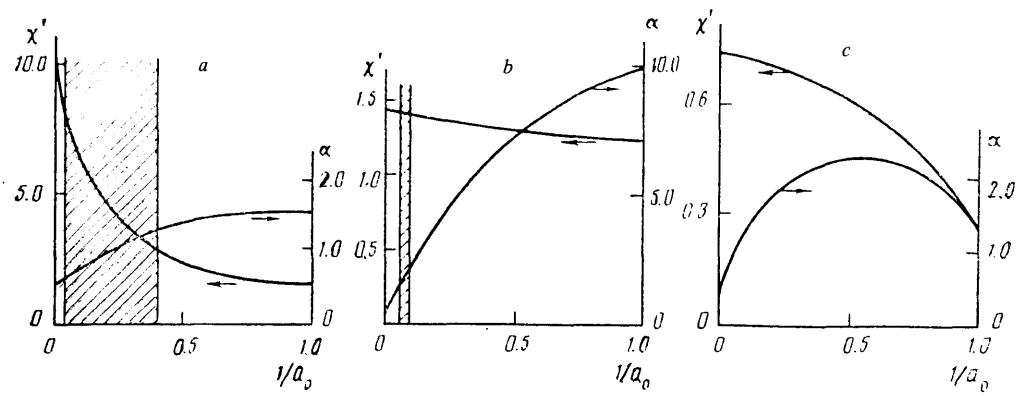


Figure 5. Permeability (or selectivity)–topology diagrams: *a*) separation of a Kr–Xe mixture on a PVTMS–PDMS block copolymer;[50] *b*) separation of an H_2–Xe mixture on a PVTMS–PDMS block copolymer;[50] *c*) a model example (gas mixture no.3 in the Table).[43]

select the optimum structure for gas-separating membranes because, for known transport properties of the initial components, they display clearly the properties of any heterogeneous structures. In the case shown in Fig.5*a* selection of the structure enables primarily the efficiency of the membrane to be controlled, altering it by an order of magnitude; the selectivity, however, is only altered by a factor of 1.5. Fig.5*b* illustrates the reverse case: the structure of the membrane controls mainly the selectivity while the efficiency remains almost constant. A more complex version is shown in Fig.5*c*. Here, as was indicated above, a change in the topology leads to extremal values of α. The region where the extremum occurs is shown clearly in the diagram. Analysis of the component functions χ' and α allows a quick estimate of, for exmaple, the loss in efficiency of the membrane as the selectivity is increased; there is also the possibility of introducing a single component function, the plotting of which requires additional information on a specific chemical-technological process.

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Methods for Obtaining Polymeric Membranes

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Methods for obtaining semipermeable polymeric membranes have been described. Various aspects of the physicochemical processes taking place during the production of membranes from polymer solutions and melts have been examined. Methods for obtaining membranes by sintering polymers, and methods for transforming continuous films and the walls of hollow fibres with continuous walls into porous membranes, have been described. Data on the preparation of composite membranes have been given. Particular attention has been paid to methods which have found practical application in technical processes for obtaining membranes as films and hollow fibres.
The bibliography contains 117 references.

CONTENTS

I. Introduction 539
II. The preparation of continuous membranes 540
III. The preparation of porous membranes 541
IV. The production of asymmetric membranes 544
V. The preparation of composite membranes 545

I. INTRODUCTION

In the present work, an attempt has been made to review the most important information on the preparation of non-ionogenic polymeric membranes. For lack of space, the review does not deal with methods for obtaining ion-exchange and liquid membranes, membranes with a relay transfer mechanism, or dynamic membranes and polymeric membranes with metallic coatings.

Membranes can be classified in different ways.[1,2] For the present purpose, it is most appropriate to classify them according to their structural characteristics. It is usual to distinguish continuous and porous membranes. Because of their technical importance, the independent types examined include asymmetric and composite membranes, in which the thin active (towards the system being separated) layers have a higher density than the remaining part, which acts as a supporting carrier. The two layers have the same chemical composition in the asymmetric membranes, and different chemical compositions in the composite membranes.

The production of membranes with a given structure is determined by the specific features of the system being separated and the mechanism of its separation. Thus continuous membranes are used to separate mixtures by the diffusion penetration of the components, and porous membranes are used to separate mixtures by the phase penetration of the components. The separating power, permeability, and stability of the operational characteristics of membranes depend on the chemical character of the polymer and on its structure, which in turn is determined by the method and conditions of preparation of the membranes, and in a number of cases by the properties of the original polymer solution or melt.

The correct choice of polymer is of considerable importance for the production of membranes for a particular purpose. An important role is played by the affinity of the polymer for the penetrating component of the mixture being separated. In particular, for the diffusion penetration of substances through a membrane, the efficiency of their sorption by the polymer acquires considerable importance. The use of block copolymers is of interest for the directed control of the sorption of gases and their diffusion coefficients. The properties of the membranes differ considerably, depending on the type of block copolymer (for a given mass ratio of the blocks). In the case of silane–siloxane block copolymers it has been shown[3] that the composition dependence of the permeability is described satisfactorily by a "disperse phase–dispersion medium" model for block copolymers of the type AB, and by an inter-penetrating polymeric network model for block copolymers of the type BAB.[4]

The treatment of amorphous–crystalline membranes with reagents bringing about their additional crystallisation with the simultaneous formation of sub-micro-pores with dimensions of ~ 1 nm also makes it possible to increase the gas permeability. As shown[5] for polyethylene–terephthalate films, the increase in permeability is brought about by an increase in the sorption of gases by the polymeric material, and this increase is different for different gases.

A sharp increase in the permeability of polymers with respect to various gases is observed when there is a specific interaction. Thus membranes of a copolymer of ethylene difluoride and ethylene tetrafluoride show an increase in their permeability with respect to ammonia during use as a result of chemical changes taking place in the polymer.[6] The permeability reaches $(0.6-1.5) \times 10^{-10}$ cm^3.cm/cm^2.s.Pa, and the separation factor reaches 5000 for the ammonia–hydrogen system, and 37000 for the ammonia–nitrogen system.

For the effective separation of liquid systems, the wettability of the membrane material by the penetrating component of the mixture being separated is of considerable importance. If the wetting angle of the membrane is greater than 90°, part of the energy is used up in overcoming the forces of surface tension at the phase boundary. kat the same time, the polymeric material of the membrane should not undergo marked swelling in the system being separated, to avoid a change in the pore dimensions and compaction of the membrane under the influence of the pressure applied to it. The last requirement applies to a lesser extent to polymers designed for the production of dialysis membranes than to polymers used in membrane processes involving the application of pressure.

In a number of cases, particularly in the separation of liquid systems by ultrafiltration, an important role is played by the redistribution of the electron density in the macromolecules, since this factor may influence the preferential sorption by the membrane of individual components of the system being separated. Since in most

cases the membranes are produced from polymer melts or solutions, it is desirable that the polymer melt without decomposing or dissolve in available solvents.

II. THE PRODUCTION OF CONTINUOUS MEMBRANES

Continuous membranes are most frequently obtained by casting from melts or by dry forming from polymer solutions.† The production of selectively permeable membranes from polymer melts does not differ fundamentally from the production of films and fibres designed for other purposes.

Fusion and crystallisation are first-order phase transformations, that is these processes are accompanied by a discrete change in the internal energy and specific volume. When a polymer melt is cooled, long-range order may appear in it, that is ordered formations, comparable in magnitude with the segments of the macromolecules and with the length of the polymer chains, may be produced. Compact formations preserved in the melts (not broken down on fusion) often act as growth centres for the crystallites in the polymer.[7]

The diffusion permeability of polymeric membranes depends on the diffusion coefficient of the penetrating substance in the polymer and on its sorption by the polymer. The maximum values of the penetration coefficients are characteristic of highly elastic flexible-chain polymers. The permeability of the polymer generally decreases with increase in the rigidity of the chains and increase in the number of polar groups.[8] A decrease in permeability is also observed when the polymers are cross-linked, although the sorption of gases changes little.[9] The permeability of membranes is influenced by the ratio of the amorphous and crystalline phases in the polymer, where the dependence is often non-linear, and also by the structure of the amorphous regions and the morphological characteristics of the crystalline formations.

A decrease in the crystallinity of the polymer usually leads to an increase in the permeability of the membranes.[10,11] An exception is provided by membranes of poly-4-methylpent-1-ene, whose density is lower in the crystalline state than in the amorphous state.[12] Up to a definite limit, the dimensions of the spherulitic formations have no significant influence on the gas permeability, which increases significantly only with further increase in the size of the spherulites, as a result of the development of micro-cracks.[13]

To decrease the crystallinity of membranes, branched polymers are used. Thus the crystallinity of branched polyethylene is 50 to 60%, whereas that of the non-branched analogue reaches 70 to 80%.[14] A decrease in the crystallinity of the polymer can apparently be brought about by marked superheating of the melt (50 to 55 K above the melting point), which leads to the formation of a completely isotropic system and to the disappearance of the crystallisation nuclei.[15]

An important role in the control of the crystallinity of the material is played by the rate of cooling of the melt.[16] If the melt is cooled rapidly to the vitrification temperaturre of the polymer, the rate of crystallisation approaches zero, and its duration tends to infinity. According to Avrami's equation:[17]

$$a = 1 - \exp(-k' t^{n_A})$$

†The terms "dry" and "wet" forming are taken from chemical fibre technology. In dry forming, the solvent is removed by evaporation, and in wet forming it is removed by mixing with a precipitant.

where a is the degree of crystallinity; k' the crystallisation rate constant; t the time; and n_A the Avrami coefficient, which varies from 1 to 4 and characterises the morphological features of the crystal formed, and also the mode of production of the crystallisation centres (thermal or athermal). For the slow formation of structures with three-dimensional order, $n_A = 4$, and for the instantaneous formation of one-dimensional structures, $n_A = 1$. Intermediate values correspond to the instantaneous formation of structures with three-dimensional order, the slow formation of structures ordered in two dimensions, and other cases.[18]

Homogeneous (continuous) membranes can be obtained by dry forming from polymer solutions by analogy with the processes involved in the production of cinematographic films and acetate textile fibre. In this case the original system (solution) does not separate into phases, but remains single-phase until the solvent is completely removed; as the solvent is removed, the viscosity of the system increaes by several orders of magnitude, and the system loses its fluidity. The increase in the viscosity as a result of the increase in the concentration of the polymer in the system can be described by the equation[19]

$$\lg \eta = \nu c^{\alpha}$$

where η is the viscosity; c the polymer concentration; and ν and α are constants which depend on the nature of the polymer and the solvent.

The rate of evaporation of the solvent influences the properties of the membranes formed. Thus when crystallising polymers are used, slow evaporation of the solvent facilitates crystallisation, often leading to a decrease in the permeability of the membranes. The rate of evaporation of the solvent depends on its vapour pressure above the solution p_1 decreases. This is observed in the first stage of the evaporation of the solvent from a liquid film or a stream of solution (in the production of membranes in the form of a hollow fibre). The difference in the chemical potentials in different layers of the solution leads to diffusion of the solvent from the inner layers, and the rate of diffusion gradually decreases, accompanied by an increase in the concentration of the polymer in the solution and an increase in the solution viscosity. For solutions with medium concentration, this process is described approximately by the equation[20]

$$Q/t = bc^{r/s}$$

where Q/t is the rate of diffusion of the solvent in the solution, and b a constant which depends on the nature of the polymer and the solvent, temperature, and other factors.

The difference in the rates of removal of the solvent from different layers of the liquid film or fibre leads to non-uniformity of the structure along the thickness of the membrane.[21] For example, in films produced on rigid supports it is possible to distinguish three layers: a compact upper layer, a loose intermediate layer, and a plane-orientated lower layer. In the production of membranes in the form of hollow fibres, the polymer molecules are oriented in the channels of the holes in the die. After the jets leave the holes, the induced orientation of the polymer is partly reduced as a result of relaxation processes, but usually it cannot be eliminated completely. The influence of orientation on the gas permeability of the polymer is indeterminate. The permeability depends on the relative quantity of cavities in the material. For example, the cold stretching of polyethylene by 297% leads to a decrease in the number of cavities.[8] There is a simultaneous decrease in the sorption, diffusion

coefficient, and permeability. On the other hand, when nylon-66 is stretched, the number of cavities increases, leading to an increase in the permeability, and this effect overlaps the influence of the increase in crystallinity. A five-fold increase in the orientation of polypropylene, although leading to loosening of the structure, a decrease in the crystallinity, and a decrease in the diffusion rate, does not bring about a significant change in the sorption and permeability.[8] A decrease in permeability was observed[22] as a result of the uniaxial stretching of polyethylene, and is attributed to the rearrangement of the spherulitic and micro-spherulitic structures in the highly oriented material and to the significant deviation from thermodynamic eqiuilibrium in the amorphous regions in the layers between the crystallites.

The dependence of the permeability of polymeric materials on the degree of biaxial stretching is complex, and in a number of cases extremal. Polyethylene–terephthalate films are more sensitive to biaxial than to uniaxial stretching. Polypropylene and polyethylene show a slight decrease in permeability at low deformations, and an increase at deformations exceeding a certain critical value. This can be attributed to the appearance of sub-micro-cracks or to recrystallisation. Polyethylene tetrafluoride, whose macromolecules are highly rigid, shows an increase in permeability on even slight biaxial orientation.[8]

All these relationships must be taken into account in the production and application of membranes. Dry forming can be used to obtain ultra-thin membranes (thickness 300–500 nm) from polymer solutions with low concentrations (0.5–2%) on a liquid surface (mercury, water). The volatile solvent should not be miscible with the liquid support.[23] The membrane formed is practically isotropic, and has a high permeability. Considerable difficulties arise, however, when these membranes are used. To avoid these difficulties, asymmetric and composite membranes have been developed, and have found extensive application.

III. THE PRODUCTION OF POROUS MEMBRANES

Porous membranes are obtained by different methods. In particular, continuous membranes can be made porous by "bombarding" them with the ions of heavy elements, for example ^{136}Xe, ^{84}Kr, and ^{40}Ar,[24] or with radioactive decay products.[25] The starting materials are continuous films of polyethylene–terephthalate, polyamide, polycarbonate, etc. When they strike the polymer film, the ions bring about cracking degradation of the polymer. The density of the breakdown brought about by the particle is proportional to the square of its electrical charge and approximately inversely proportional to the square of its velocity. Since the maximum possible critical rate of loss of energy by the particle in the polymer dt/dx increases with increase in the atomic mass of the particle, there exists a lower limit of the mass of the ions capable of forming "traces". The beam of ions is collimated to ensure that the direction of the "traces" is perpendicular to the membrane surface. The film treated with the ions is subjected to strong ultraviolet irradiation to intensify the subsequent etching, which is carried out using solutions of alkalis or acids, depending on the nature of the polymer. During etching, pores are formed in the film; the form of the pores depends on the ratio of the rate of extraction of the material along the axis of the "trace" v_t to the rate of extraction of the material from the undamaged surface v_s. The form of the pores is close to cylindrical when $v_t > v_s$; when $v_t \simeq v_s$, a conical depression is formed in the film. These membranes, which are usually called nuclear filters, are most widely used in microfiltration processes.

Another method for converting continuous into porous membranes involves swelling the original membrane, with a cryptoheterogeneous structure, and then fixing the resulting pores.[26]

Methods for obtaining porous membranes by stretching continuous membranes under strictly controlled conditions have been used increasingly in recent years. These processes can be carried out in two ways. One involves the use of the familiar Rebinder effect. Stretching continuous films in adsorption-active media makes it possible to produce membranes with a developed system of continuous connecting pores.[27] This principle has been used, for example, to obtain a porous hollow polyethylene fibre.[28] For this purpose, the fibre was subjected to thermal treatment for 30 min at 90–120°, after which it was kept in trichloroethylene or perchloroethylene at a temperature above the vitrification temperature of the polymer. The fibre was then stretched by 200–300%, and then subjected to thermal fixation at 85–120°, when it was allowed to shrink by 5%. A similar process has been carrried out for films of polytetrafluoroethylene[29,30] and polyethylene–terephthalate.[31] In particular, when films of vitreous polyethylene–terephthalate were stretched by 200% in n-propanol, the quantity of pores was brought to 3.2×10^{12} cm^{-2}, with average dimensions of $\sim$4.6 nm.

Continuous membranes of crystallising polymers can also be made porous without using adsorption-active media.[32–37] The process usually involves the stages of preliminary heating of the material, stretching to produce a system of pores in the material, and thermal fixation of the porous structure. The formation of pores when the membrane is stretched can be represented as an increase in the distance between the lamellae; when an external force field is applied to the system, the "through" chains are partly "drawn out" from the lamellae into amorphous region.

The degree of stretching influences the pore dimensions.[32] The stretched membrane is subjected to thermal fixation at the temperature of the preliminary heating or a slightly higher temperature. The thermal fixation is carried out under slight tension, which controls the partial shrinkage of the material. Since this is accompanied by the relaxation of a considerable proportion of the internal stresses, the membrane subsequently does not undergo appreciable shrinkage deformation, and its porosity is preserved.

This method of producing porosity has been most widely used in the preparation of hollow fibres of polyalkenes,[33–36] poly-*p*-phenylene sulphide,[37] etc. Porous polyalkene membranes can be used to separate gas mixtures as a result of the difference in the rates of penetration of the individual components through the pores by a Knudsen flow mechanism. These materials appear promising for removing contaminants from liquid fuel and oils by ultrafiltration, and also for carrying out membrane distillation, a process in which increased interest has recently been shown.[38,39]

When porous polyalkene membranes are used in the separation of aqueous systems, the polymer is often made hydrophilic, for example by treating it with sulphuric acid or by grafting hydrophilic monomers.[40] Membranes can be made hydrophilic by treating them with a gas mixture containing SO_2 and F_2.[41]

One method of producing porous membranes is by sintering powders or by calendering finely dispersed polymers. A detailed analysis and description of the processes involved in the production of micro-filtration membranes by this method have been given.[42] It is particularly appropriate to use this method with polymers which cannot be brought into the viscous-flow state by fusion or solution.

The primary example of polymers of this kind is polytetrafluoroethylene, which has a high chemical stability and can withstand temperatures above 200°, Polytetrafluoroethylene membranes are obtained by sintering its powder in pure form[43–45] or in mixtures with binding agents, including other fluorine-containing polymers. A number of petroleum products have been used as binding agents.[46,47] The mechanical strength of polytetrafluoroethylene membranes not containing a binding agent is usually insufficient. To eliminate these disadvantages, membranes with a fibrous filler are prepared.[2] These membranes, with a thickness of 0.12–0.15 mm, have pores with dimensions up to 500 Å. They are hydrophobic, and therefore impermeable to water at low pressures (up to 1.2 MPa).

Examples of the production of membranes by sintering are also known for other polymers, in particular polyalkenes, with the introduction into the mixture of materials which can be removed by water, for example starch.[48] The sintering is carried out at a temperature above the vitrification temperature of the polymer. Interdiffusion of the macromolecules of the particles in contact with one another takes place. The adhesion of the particles leads to a decrease in the specific surface of the system, and hence to the liberation of free energy:[42]

$$\Delta E = \sigma_{pa}(1/r - 1/R) \qquad (1)$$

where σ_{pa} is the surface tension of the polymer at the boundary with air, r the radius of the contact surface, and R the radius of the particle.

During the technical process, it is extremely important not to allow complete merging of the particles, since this naturally leads to closure of the pores. It is important to stop the process at the first stage of the sintering. The duration of this stage (τ) for a number of systems can be determined if the familiar Frenkel' equation[49] is written in the form: $\tau = 2\pi r^2\eta/3R\sigma_{pa}$, where η is the viscosity of the melt.

The method of obtaining porous membranes by separating polymer solutions into phases has been most widely used. This method opens up extensive possibilities for the directed control of the structure and operational properties of membranes.

Solutions of macromolecular compounds are not ideal. For these solutions, the following relationship applies: $\Delta G_{rs} = \Delta G_i + \Delta G^E$, where ΔG_{rs} is the free energy of the real solution, ΔG_i the free energy of the ideal solution, and ΔG^E the excess free energy. Positive values of the deviation ΔG_{rs} correspond to poor miscibility of the components.[50] When ΔG^E reaches $\sim 0.5\ RT$,[51] the solution separates into phases.

The decomposition of polymer solutions into phases can take place by two mechanisms—nucleation and spinodal. Analysis of the equilibrium diagram of a polymer–solvent system (Fig.1) leads to the following basic postulates.[52] The region lying above the binodal corresponds to a thermodynamically stable single-phase solution. This region is characterised by the inequality $(\partial^2 g/\partial x^2)_{pT} > 0$, where g is the average free energy of the system, and x the molar concentration of one of the components. The region lying between the binodal and the spinodal corresponds to a metastable state of the system. For the range of metastable states, the inequality $(\partial^2 g/\partial x^2)_{pT} > 0$ is again applicable. In this region, the diffusion fluxes of the components are directed in such a way that they decrease the fluctuations. The formation of a new interface is energetically unfavourable, and the work of formation of the nuclei of the new phase provides a measure of the metastability of the solution.[52] Thus the system is unstable only with respect to heterophase fluctuations exceeding a certain critical value.[53] If this critical value is exceeded, a spontaneous increase in the fluctuations takes place.

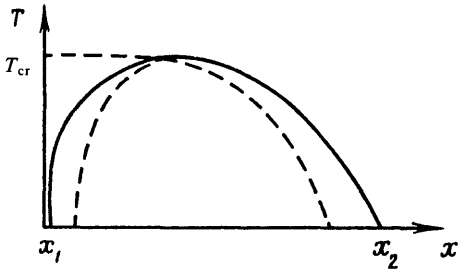


Figure 1. Equilibrium diagram of a polymer–solvent system (continuous line–binodal, broken line–spinodal): T–temperature, x_1–concentration of the solvent, x_2–concentration of the polymer.[52]

As the nuclei of the new phase are formed, the concentration of the polymer in the solution decreases. At the same time there is an increase in the coefficient of self-diffusion of the macromolecules,[54] and it follows from scaling theory that this increase for concentrated solutions shows a cubic dependence on the mass fraction of the polymer in the solution. The increase in the coefficient of self-diffusion of the macromolecules leads to the growth of the nuclei of the new phase. The rate of the formation and growth of the nuclei depends on the degree of supersaturation of the solution. The degree of supersaturation in turn can be controlled by changing the temperature, using precipitants with different compositions, and changing the concentration of the polymer in the original solution. The development of the growth of the nuclei of the new phase when there is a sufficient quantity of polymeric material in the system leads to the nucleation breakdown of the polymer solution into phases, that is to the formation of a polymeric framework including regions of a phase with a low polymer concentration (this is usually a mixture of the solvent and the precipitant in which a small quantity of the polymer, mainly its low-molecular-weight fractions, is dissolved).[55] The polymeric framework formed as a result of the breakdown of the solution into phases is subjected to syneretic contraction, as a result of which it becomes more compact, with the simultaneous partial separation of a liquid phase. The polymer is converted from a highly fluid into a highly elastic (and sometimes vitreous) state.

On the spinodal, the work of formation of the nuclei of the new phase is equal to zero; the equation of the spinodal is $(\partial^2 g/\partial x^2)_{pT} = 0$.[52] Under the spinodal lies a region corresponding to a thermodynamically unstable state of the system. This state corresponds to the inequality $(\partial^2 g/\partial x^2)_{pT} < 0$. In the initial stage of the spinodal decomposition of the system into phases in the homogeneous solution a set of concentration fluctuations is produced, and these can be regarded as a set of sinusoidal waves with a fixed length λ equal to the dimensions of the structures formed. The fluctuations may not reach the critical value, as in the nucleation process of breakdown into phases. Subsequently, at the points where the fluctuations are

produced, as a result of the existence of a component flux directed against the concentration gradient, micro-regions of the heterogeneous structure are enriched in these components, and begin to coalesce.[56] The temperature at which the rate of formation of the interconnected micro-regions of phase separation is a maximum corresponds to a definite composition. If the volume fraction of one of the components is greater than 15%, then in the final stage of the process, the coalescence initiated by hydrodynamic factors ensures that each phase is connected.[51] At this stage, the dimensions and composition of the structures may be the same as in the nucleation mechanism of the breakdown, that is two phases with concentrations of a given component x_1 and x_2 may coexist in equilibrium. When the change in temperature is rapid, however, a non-equilibrium system with a matrix (continuous) phase may be preserved.[57] The structures formed in this case differ from those produced in nucleation breakdown. In the coalescence process, the initially spherical particles form either cellular or network structures,[58,59] which form the basis of the highly porous membranes.

The theory of spinodal decomposition applied to polymeric systems was developed by De Gennes.[60] Spinodal breakdown has been studied experimentally by a number of workers.[56–59,61,62]

In practice, semipermeable membranes are produced mainly by the breakdown of solutions into phases by the nucleation mechanism. The original (forming) solution is converted to the metastable state by changing either its temperature or its composition. The latter is achieved either by evaporating the solvent from the three-component solution containing the polymer, the solvent, and the precipitant (spontaneous gel formation method) or by using the method of wet forming to obtain the membranes.

The method of spontaneous gel formation is widely used to obtain film membranes for ultra-filtration and micro-filtration. Its essential features are as follows. A solution of the polymer is prepared in a mixture of a solvent with a non-solvent, which should be less volatile than the solvent. The solvent is then evaporated from a film of the liquid deposited on a stationary or moving support. As a result of the change in the composition of the system, it breaks down into phases with the production of a gel which forms the basis of the highly porous membrane.

To analyse the processes taking place, it is appropriate to examine the equilibrium diagram of a three-component polymer–solvent–non-solvent (precipitant) system, represented in general form in Fig.2.[63] The solid phase (polymer) can be isolated from the solution with the composition A by different methods. For systems with an upper critical temperature of mixing, $T_1 > T_2$, and for systems with a lower critical temperature of mixing, $T_1 < T_2$. If the solution A contains a solvent whose vapour pressurre is higher than that of the precipitant, the decomposition of the solution into phases takes place as a result of the evaporation of the solvent. At the point B_2, the system loses its homogeneity, and decomposes into phases with compositions x_1 and x_2, after which, as a result of the evaporation of the solvent and the precipitant, it acquires the composition P. If however the precipitant is more volatile than the solvent, the composition of the system changes along the path AGP, and the system remains homogeneous throughout.

To obtain membranes by the wet forming method, the original system is enriched in the precipitant by diffusion processes, with a simultaneous decrease in the concentration of the solvent. At the point B_1 below the temperature T_2 (or at the point B_1' below the temperature T_1), the solution breaks down into phases with compositions x_1 and x_2 (below the temperature T_2) or x_1' and x_1' (below the temperature T_1). On subsequent "elution" of the solvent by the precipitant, the system arrives at the composition C_1 or C_2, and then, as a result of drying along the paths C_1P or $C_1'P$, at the composition P.

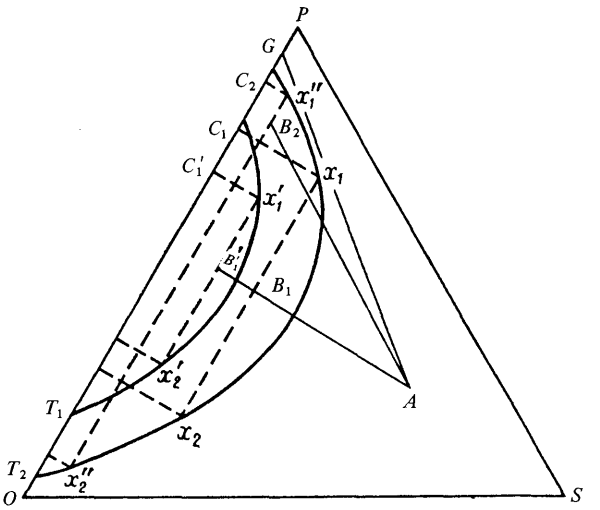


Figure 2. Equilibrium diagram of a three-component system (for explanation see text).[63]

Analysis of the diagram shows that for systems with an upper critical temperature of mixing, the concentration of the polymer in the framework phase increases with decrease in the temperature of the phase separation. This is important for controlling the parameters of the porous structure of the membranes.

In addition to thermodynamic factors, it is also necessary to take account of kinetic factors, which have a considerable effect on the structure and properties of the membranes. For example, the change in composition along the path AB_2C_2P may take place so rapidly that the breakdown of the system into phases cannot take place.[64] Because of the very high viscosity of the gel, the conversion of the system from the heterogeneous to the homogeneous state on the section C_1P (paths $C_1'P$; C_2P) is extremely difficult, so that after the removal of the precipitant from the gel, the system may remain heterogeneous for an unlimited time.

One of the most widely used technical methods for controlling the degree of supersaturation of the forming solutions is by using precipitant baths with different composition, in particular with different ratios of the precipitant and the solvent. In practice, baths containing a small quantity of solvent are called "hard", and baths containing a large quantity of solvent are called "soft". The use of hard precipitant baths, which bring about extensive supersaturation of the solution, leads to the production of a large quantity of nuclei of the new phase in the system and to their rapid growth. Steric hindrance, however, restricts the growth of the particles of the new phase. As a result, a membrane with fine pores is formed. A similar effect can be achieved by increasing the polymer concentration in the solution and by changing the temperature of the system.

The influence of these factors on the structure and properties of membranes obtained from cellulose esters has been studied by many workers.[65–74]

In the study of the wet forming of membranes from aromatic polyamides, polyacrylonitrile, and other polymers it has been shown[75,76] that the morphological characteristics of the membranes vary considerably, depending on the polymer precipitation conditions. Soft precipitation of the polymer from highly concentrated solutions gives a regular spongy material. Hard precipitation of the polymer from solutions with a low concentration gives a membrane permeated by large rod-shaped pores. In the formation of these pores, a decisive influence is assigned[77–80] to local convection currents in the liquid, arising as a result of the exothermic character of the interaction of the solvent with the precipitant.

Breakdown of solutions into phases by the spinodal mechanism is as yet very rarely carried out in technical practice. In this connection, mention may be made of the process carried out by the West German firm "ENKA Membrana" for obtaining tubular and capillary membranes, known by the trade name "Accurel", from solutions of polypropylene in an organic oil (other solvents may also be used). The heated solution is extruded through a specially designed die, after which it is rapidly cooled. This gives a highly porous isotropic membrane, which can be used successfully as a micro-filter.[81]

IV. THE PRODUCTION OF ASYMMETRIC MEMBRANES

The different conditions of formation of the structure of the films and fibres in different layers leads to the formation of asymmetric membranes. Since the preparation of the first asymmetric membranes,[82,83] the most widely used but not the only method for obtaining them has been by dry–wet forming. In this process, the solvent is partly evaporated from the surface layer of the solution, after which the solution (in the form of a liquid film or filament) is placed in a precipitating bath, where it breaks down into phases. As a consequence of the higher concentration of the polymer in the surface layer, a compact polymeric sheath is formed on the surface of the membrane, giving it its high separating power. At the same time, the loose polymeric matrix formed from the layer with the lower concentration ensures that the membranes are highly permeable to the penetrating components of the system being separated. The active (selective) layer usually corresponds to a small fraction of the thickness of the asymmetric membrane. The absolute thickness of the active layer varies from 0.1 μm^2 to 0.25 μm,[84,85] although thicker layers up to 4 μm are also encountered.[10]

The parameters of the process of the partial evaporation of the solvent from the surface of the liquid film or filament (chiefly the rate of evaporation) play an important role in the production of the structure of the asymmetric membrane.[86,87] The lower the rate constant of the evaporation of the solvent, the higher the permeability of the membranes for a given selectivity. Since the rate constant of the evaporation of the solvent depends on several factors (the concentration of the solvent vapour in the evaporation zone, temperature, etc), it is possible to obtain membranes with identical properties for different parameters of the technical process. A necessary condition, however, is a constant value of the solvent evaporation rate constant, which has an optimum value for each composition of the forming solution.

An important role in the formation of asymmetric membranes is played by surface phenomena.[88] If the surface tension σ_1 at the boundary between the solvent and air containing the solvent vapour is lower than the surface tension σ_2 at the boundary between the solution and air containing the solvent vapour, then the surface of the forming solution in contact with air is enriched in the solvent, and the polymer is sorbed on the support, forming an asymmetric membrane with the compact layer in contact with the support. If however $\sigma_1 > \sigma_2$, then the surface in contact with air is enriched in the polymer, and after the breakdown of the solution into phases, the compact selective layer is formed on this surface.

Since the structure and properties of the membranes depend on the structure of the forming solutions, the rates of their breakdown into phases, and the surface properties of the system, the importance of the correct choice of solvent is obvious. Frequently, the solvent used is a two-component mixture, one of whose components is an effective solvent, while the other is a swelling agent.

A noteworthy procedure developed by a number of workers[89–93] involves the selection of the solvent from the magnitude of the Hildebrand solubility parameter δ. It is known[94,95] that $\delta = (\Delta E/v)^{1/2}$, where v is the molar volume, ΔE the energy of cohesion, $\Delta E = \Delta E_d + \Delta E_p + \Delta E_h$, and ΔE_d, ΔE_p, and ΔE_h the components of the energy of cohesion due to the action of dispersion forces, polar forces, and hydrogen bonds respectively.

From the equations given it follows that $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$.

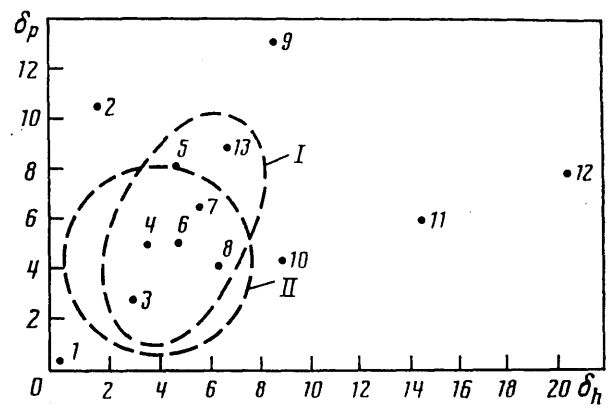


Figure 3. Solubility diagrams of cellulose acetate (*I*) and polysulphone (*II*):[89] *1*) carbon tetrachloride, *2*) ethylene carbonate, *3*) methylene chloride, *4*) acetone, *5*) dimethyl sulphoxide, *6*) dimethylacetamide, *7*) dimethylformamide, *8*) acetic acid, *9*) formamide, *10*) ethanol, *11*) glycerol, *12*) water, *13*) mixture of acetone and formamide (6:4).

The range of solubility of substances can be represented in the form of a sphere on coordinates $\delta_d - \delta_p - \delta_h$.[96,97] Since for most substances the values of δ_d are similar,[96] it has been proposed that the mutual solubility of substances be characterised using two-dimensional diagrams on coordinates $\delta_p - \delta_h$ (Fig.3). The action of weak forces can be taken into account by a generalised parameter $\delta_v = (\delta_d + \delta_p)^{1/2}$.[98] The range of solubility can then be represented on coordinates $\delta_v - \delta_h$. The fraction of each component of δ can be

represented as follows:

$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h}; \; f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h}; \; f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h}$$

The range of solubility can then be represented on a triangular Hashimoto diagram[93] (Fig.4).

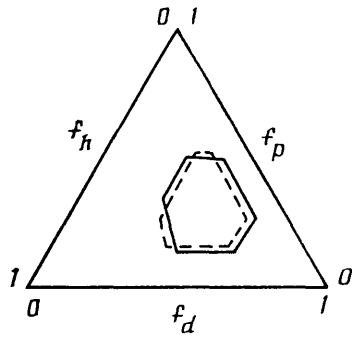


Figure 4. Diagram of secondary cellulose acetate (continuous line) and cellulose triacetate (broken line) on Hashimoto coordinates. For explanation see text.[93]

To obtain a highly permeable asymmetric membrane, the orioginal solution should satisfy the following requirements:[89] all the components of the dissolving mixture should be compatible with the precipitant; the composition of the solution before the breakdown into phases should correspond to the range lying at the solubility boundary; the concentration of the structure-formation centres in the solution before the breakdown into phases should be high, to ensure the rapid precipitation of the polymer; when the volatile component of the dissolving mixture is removed, the solubility of the polymer should decrease.

The breakdown of the forming solution gives the so-called "primary gel". To give the membrane a compact structure, it is subjected to annealing involving thermal treatment in a liquid medium, which produces shrinkage deformations in the polymeric material. A necessary condition for effective shrinkage is the devitrification of the polymer.[63] For cellulose acetate in an aqueous medium, the devitrification temperature is 90–95°.[99] Thus the annealing temperatures of 75–85° given by Brock[100] for cellulose acetate membranes are too low.

The shrinkage of the polymer takes place to a greater extent in the surface layer than in the loose matrix. This is due to the higher concentration of stresses in the surface layer of the membrane as a result of the more rapid precipitation of the polymer on the surface of the liquid film, compared with the volume. Annealing leads to an increase in the salt-retention power of membranes designed for reverse osmosis, and increases their water permeability.

The membranes obtained in this way have an ultraporous structure, and are extensively impregnated by liquid. When the liquid evaporates, the forces of capillary contraction bring about closure of the pores, as a result of which the membrane may lose phase permeability. To avoid this, the membrane is usually impregnated with glycerol, a liquid with a low volatility. This membrane retains its operational properties for a time interval sufficient for the preparation of the separating module.

Asymmetric membranes are used for the separation of both gas mixtures and mixtures of solutions by reverse osmosis and ultrafiltration. An example is a gas-separating membrane of polyvinyltrimethylsilane, which has permeability coefficients with respect to O_2 and N_2 of 15.0 x 10^{-15} mole.m/m^2.s.Pa and 3.5 x 10^{-15} mole.m/m^2.s.Pa respectively.[1] Asymmetric membranes are widely used as ultra-filters with molecular-mass retention limits from 1000 to 300 000, and also to separate solutions by reverse osmosis.[77–87]

V. THE PRODUCTION OF COMPOSITE MEMBRANES

In recent years there has been an increase in interest in the production of composite membranes. This development is regarded as particularly promising.[101] Composite membranes are obtained by depositing a layer of another polymer on a porous base. The first successful attempts were made in the early nineteen-seventies,[102] and in recent years the method has been developed on the industrial scale. Membranes with unique properties have been obtained. It is suggested that composite membranes undergo less deformation on the application of pressure, compared with asymmetric membranes. Polymers with unique properties can be used to obtain the selective layer of composite membranes. Since the coating is thin, the quantity of polymer used for the production of the membrane is small, so that the cost of the polymer is not usually a limiting factor.

Several methods can be used to obtain composite membranes. A popular method involves the deposition of the active layer by plasma polymerisation in a glow discharge.[103–108] Various organic compounds can be subjected to plasma polymerisation, including compounds which cannot be polymerised by ordinary methods, for example benzene. In the glow discharge, benzene is apparently converted into acetylene, which then polymerises.[109] The monomers used include acetylene, allylamine, 4-vinylpyridine, N-vinylpyrrolidone, 4-picoline, 4-ethylpyridine, 4-methylbenzylamine, 3,5-dimethylpyridine, and other compounds.[109]

Plasma polymerisation can be carried out by electrodeless and electrode methods. To establish the electrodeless discharge, the discharge tube is placed inside a solenoid, through which the electric current passes. The discharge takes place when definite values of the current strength and frequency have been reached. The polymer formed is deposited on a porous support in the zone of the glow discharge. The supports used include ultra-filters with pore dimensions of ~25 nm,[109] hollow fibres, porous glass, and other porous materials.

When the electrode method is used, the polymer is deposited on the electrodes, which may be porous plates; the distance between the plates is 5–40 mm.[109] Before the stream of monomer is supplied, the air is evacuated from the plasma polymerisation chamber to a residual pressure of ~10^{-1} Pa. The monomer vapour is then introduced into the chamber to a pressure of 10 Pa, after which an inert gas is added to increase the pressure to 25 ± 5 Pa. A high-frequency generator is then used to create a glow discharge, which brings about the polymerisation of the monomer.

The water permeability of the membrane obtained naturally depends on the hydrophilic character of the polymer formed. Thus if methacrylic acid is used as the original monomer, the water permeability of the membrane is 5.85 x 10^{-6} m^3/m^2.s, and when vinyl

acetate is used, the water permeability is 2.02 x 10^{-6} $m^3/m^2.s$, and the selectivity towards sodium chloride is almost the same in both cases. A highly selective and highly permeable membrane for reverse osmosis can be obtained by treating a porous polyacrylonitrile membrane with a plasma with the introduction of He, H_2, and O_2 into the discharge zone.[110] This gives a cross-linked surface layer containing $-OH$, $>C=O$, and $>NH$ groups.

Composite membranes are also obtained by the vacuum deposition of a thin (0.05 μm) active polymer layer on a porous support,[111] and also by depositing polymer solutions with a low concentration on a porous base and then evaporating the solvent.[112,113] In the last case, the adhesion interaction between the polymer and the material of the support is of considerable importance. The thermo-dynamic characteristic of the adhesion is the loss of free energy per unit surface area of contact between the solids in contact. The work of adhesion is given by

$$W_a = \sigma_{sa} + \sigma_{la} - \sigma_{sl}$$

where σ_{sa}, σ_{la}, and σ_{sl} represent the surface tension at the solid base–air, solution–air, and solution–solid base boundaries respectively. This equation shows that to improve the adhesion of the solution to the porous base, it is necessary to select systems for which the surface tension at the boundary with one another is a minimum. Composite membranes obtained by depositing polyelectrolyte complexes on a porous base have found practical application.[114]

Methods for obtaining composite membranes by depositing on a porous base a thin film formed as a result of interphase polycondensation are of considerable interest.[115–117] This method has been used to obtain membranes for reverse osmosis with a selectivity (with respect to sodium chloride) of up to 99% with a specific permeability of 0.40–0.55 $m^3/m^2.d$.[117]

In the near future, technical development will be directed towards the search for new polymers for the production of highly effective gas-separating membranes and membranes with functions analogous to those of biological membranes.

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Selectively Permeable Polymers and Gas-separation Membranes: Structure and Transport Properties

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The relationship between the permeability coefficients and the sorption and diffusion properties of highly elastic and vitreous polymers has been examined. The concept of free volume can be used to interpret the characteristics of transport not only in highly elastic but also in vitreous polymers. The properties are discussed of the basic polymeric materials of gas-separation membranes; heterophase polymeric systems such as block copolymers and polymers with liquid-crystalline additives and additives undergoing specific interaction, and also quasi-liquid membranes with components facilitating the transport of gases. The bibliography contains 84 references.

CONTENTS

I. Introduction 549
II. Diffusion and free volume in polymers 549
III. Vitreous polymers—materials for gas-separation membranes 553
IV. Heterophase polymer membranes 555

I. INTRODUCTION

The considerable progress made in the last ten years in the field of membrane gas-separation has been the result of the development of a number of membranes characterised by high efficiency and selectivity combined with stability of their properties in the media being separated. A high efficiency can be achieved by producing a definite "architecture" of the membrane as a polymeric solid or by selecting for the membrane a polymeric material characterised by high diffusion and sorption parameters. Most frequently, these two approaches are combined.

The gas-permeability coefficients of polymers may differ by 5–6 orders of magnitude, depending on their structure, whereas for comparison, in liquids, the values vary by only 1–2 orders of magnitude. This is due to the varied structural characteristics of the polymeric materials and the marked influence of the structure of the polymer on the rate of gas transfer. It is thus possible to ensure that the polymeric membranes have the required permeability and selectivity by influencing the structure of the polymer. At the same time, a characteristic compensation effect has been shown to exist: the most selective polymers have a low permeability, and highly permeable polymers are insufficiently selective or have poor mechanical and film-forming properties.[1-3]

The traditional approach to the analysis of the permeability and selectivity of non-porous gas-separation membranes involves the resolution of the diffusion and thermodynamic components of the permeability coefficients P_i and the separation factors $\alpha_{ij} = P_i/P_j$:

$$\alpha_{ij} = P_i/P_j = \sigma_i D_i/\sigma_j D_j = \alpha_{ij}^{\sigma}\alpha_{ij}^{D} \qquad (1)$$

The wide range of variation in the gas-permeability coefficients of polymers, noted above, is determined chiefly by the range of their diffusion properties. The sorption parameters, characterising the thermodynamic component of the permeability coefficient, differ to a much smaller extent for different polymers. It is traditionally assumed that the driving force of the mass transfer of simple gaseous molecules, and the concentration or activity gradient, is due to van der Waals intermolecular interaction. At the same time, a marked and selective increase in the permeability may be expected if any components of the mixture being separated undergo stronger specific interactions with the membrane material (electron donor–acceptor interactions, reversible coordinate bonding in a complex, and hydrogen bond formation).

With allowance for these characteristics of mass transfer in membranes and the requirements which they must satisfy, attention will subsequently be concentrated on the progress made in the development and application of polymeric materials in gas-separation membranes, and an attempt will be made to indicate the most promising apparent routes for the development of membrane science.

II. DIFFUSION AND FREE VOLUME IN POLYMERS

1. Highly Elastic Polymers

Polymers with high diffusion coefficients are attracting attention as materials for selectively permeable gas-separation membranes. The diffusion coefficients of gases depend on various properties of the polymer—density, presence and frequency of cross-linkages, degree of crystallinity, nature of the substituents, nature of the interchain interactions, and many others, but a direct correlation between these characteristics and the diffusion coefficients of gases can be observed only for a limited number of structurally similar series of polymers. With wide variation in the chemical character of the polymers, the diffusion coefficients show a statistically significant correlation only with the vitrification (glass) temperature T_g or the difference between the temperature of the measurement of the diffusion coefficient T_m and the glass temperature, $T_m - T_g$. This difference is sometimes regarded as a measure of the kinetic rigidity of the macro-chain. The relationship between the diffusion coefficients D at a given T_m and the glass temperatures

$$\lg D = A + BT_g, \quad (B<0)$$

was first noted in Ref.4. In Ref.4, however, this relationship was established only for a limited number of combinations of the diffusing substances and polymers with $T_g < 298$ K (rubbers and

partly crystalline polyalkenes). The universal character of Eqn.(2) for the highly elastic range was subsequently confirmed[5] by an analysis of published data[6,7] for a large number of polymers and gases. Fig.1 shows that with increase in temperature in the highly elastic range (left-hand branches of the curves), both the diffusion coefficients and the permeability coefficients decrease.

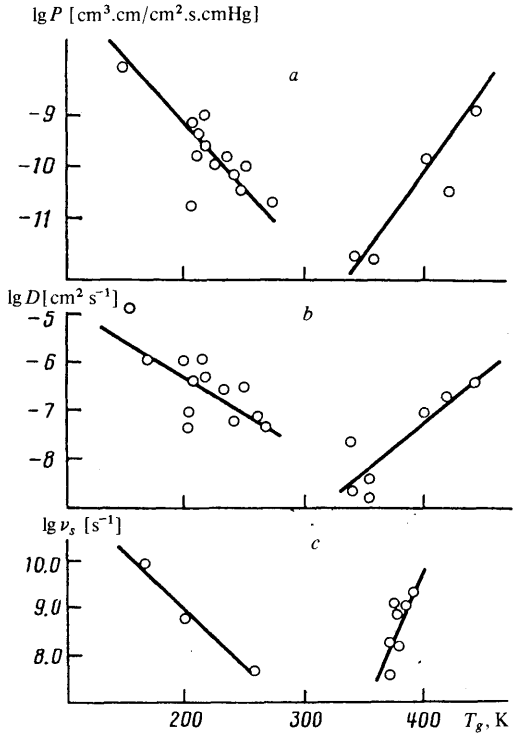
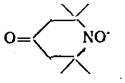


Figure 1. Correlation of the permeability coefficients of nitrogen (*a*), the diffusion coefficients of nitrogen (*b*), and the frequencies of rotation of the spin probe



ν_s (*c*) with polymer glass temperatures (from published data[6,7]).

The coefficient of translational diffusion of a gas in a polymer is an integral quantity, which may depend both on the local properties of the polymer and on its morphology (the sinuosity of the diffusion paths in the membrane, the presence of supermolecular structures, etc.). It is therefore extremely interesting to note the analogous decrease, with increasing T_g in the highly elastic range, in the coefficients of rotational diffusion of spin probes in polymers[5] (Fig.1). This shows that the observed decrease in D is related chiefly to the local mobility of the polymer chains. The fact that the diffusion coefficients of gases in rubbers, like the parameter of the Williams–Landel–Ferry equation a_T,[8] can be expressed as a single-valued function of T_g or the difference $T_m - T_g$ agrees with the view that the diffusion of gases in polymers at $T_m > T_g$ is determined chiefly by the segmental mobility

Since the free volume in rubbers is predominantly fluctuational in character, it is not surprising that different versions of the theory of free volume have been used successfully to describe the diffusion of gases in polymers at temperatures above T_g. The theory of free volume is based on the view that in a polymer, as in a liquid, there exists a free volume, whose elements, as a result of the random movement of the kinetic units making up the polymer, are displaced in space, and this makes possible the diffusion of small dissolved molecules or the viscous flow of the macromolecules in the polymer. According to the Cohen–Turnbull model of the free volume,[9] the diffusion coefficient can be represented as

$$D = A\mathscr{P}(v^*, v_f) = A \exp(-\gamma v^*/v_f) \qquad (3)$$

where $\mathscr{P}(v^*, v_f)$ is the probability that a molecule with a volume v^* enters a cavity with a volume $v > v_f$; γ is the overlap coefficient of the elements of the free volume, $0.5 < \gamma < 1$ (for simplicity, it can be taken as equal to 1); and A a constant.

In this simple form, however, the model cannot easily be used for the numerical estimation of diffusion coefficients in polymers. Various modifications of the model,[10–12] differing in the ways in which the dependence of v_f on temperature and the concentration of the diffusing substance is given, make it possible to use the thoery to describe the diffusion of organic solvents in rubbers. Subsequent refinement of the model of free volume led to the equation:[10,13,14]

$$D = RTA_d \exp(-B_d/v_f) \qquad (4)$$

where B_d characterises the volume of the substance diffusing, and A_d is a constant.

In this equation, the free volume v_f is given as a function of the temperature and pressure, that is it depends on the coefficient of thermal expansion of the polymer α and its compressibility β, and on a coefficient δ which allows for the influence of the diffusing substance on v_f (that is plasticising effects). Since the values of α and β for many polymers are known, for a complete description of the diffusion of gases it is sufficient to know the parameters A_d, B_d, and δ. This has been demonstrated for the transfer of CO_2, CH_4, C_2H_4, and C_3H_8 through polyethylene membranes at high pressures. The dependence of the permeability coefficient on the pressure (p_m) can be described by the equation:[14]

$$\ln \bar{P}(p_m) = \ln[\sigma_0 RTA_d \exp(-B_d/v_f)] + (B_d/v_f^2)(\delta\sigma_0 - 2\beta)p_m \qquad (5)$$

where $p_m = 1/2(p_1 + p_2)$, p_1 and p_2 are the pressures below and above the membrane respectively, and σ_0 the solubility coefficient of the gas in the polymer.

The traditional approach in the determination of the parameters of the free volume model requires a study of the diffusion in the polymer of gaseous probe molecules with different dimensions, that is the solution of the inverse diffusion problem. It should be noted that the integral free volume $V_f = v_f N$ can also be determined independently from data on the viscosity and the thermal expansion, crystallographic data, etc. At the same time, in the case of the diffusion of gases in polymers, the size distribution of the elements of the free volume is more important. This can be estimated using probe methods, which make it possible to study the behaviour in the polymer of probes of different character and dimensions, sensitive to those characteristics of the free volume which influence the diffusion of gas molecules.

Fig.2 shows the correlation between T_g and the free volume determined by the positron annihilation method[15] in the disordered regions of polymers $(v_f)_i$. Comparison of Figs.1 and 2 shows that the diffusion and permeability coefficients on the one hand, and the

free volume $(v_f)_i$ on the other, decrease in the same way with increase in the glass temperature in the highly elastic range of the polymer. This shows that the values of $(v_f)_i$ determine the diffusion coefficients of gases in rubbers in accordance with the equations of the theory of free volume. In particular, assuming that the process of gas diffusion involves chiefly the free volume in the disordered regions, and substituting $(v_f)_i$ in Eqn.(3), it is possible, from a comparison of the parameters of this equation with the dimensions of the molecules of the diffusing gases, to conclude that the geometry of the elements of the free volume in rubbers is cylindrical, in agreement with the assumed geometry of the segment of the polymer chain. It should also be noted that as T_g approaches T_m, the free volume $(v_f)_i$ decreases to a low value. This shows that the measured free volume in rubbers is sensitive to the segmental mobility.

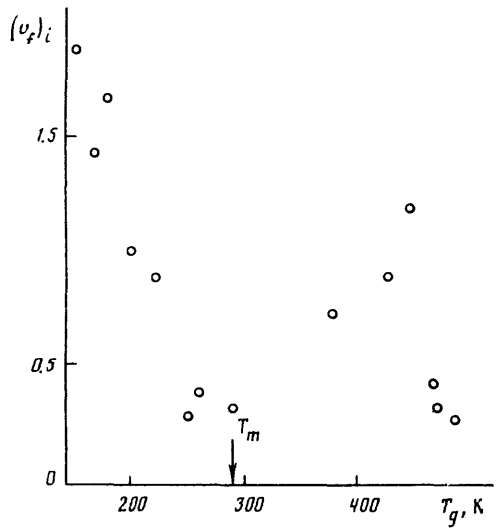


Figure 2. Correlation between the free volume $(v_f)_i$ and vitrification temperatures of polymers.[15]

At temperatures appreciably lower than T_g, the translational mobility of particles with low molecular weight is determined by the α-relaxation processes in the polymers. The small-scale† mobility in a polymer, which is often interpreted as β-transitions, is apparently appreciable close to T_g; in the highly elastic range, its contribution is small compared with that of the segmental mobility. The experimental data making it possible to estimate the role of small-scale mobility in the vitreous range will be examined below.

†The term small-scale mobility is usually employed to denote the vibrations and rotations of small groups in a polymer, which are preserved at temperatures both above and below T_g. Information on these motions in a polymer (for example the rotations of the phenyl group in polystyrene or of the methylene group of the main chain of polyvinyl chloride) can be obtained by NMR.

Among highly elastic polymers, the highest diffusion and permeability coefficients are observed for polydimethylsiloxane (PDMS) and other siloxanes differing from PDMS in the substituents on the silicon atom of the main chain (alkyl, phenyl, etc.). Polydimethylsiloxane has a lower glass temperature (150 K) than other polymers. The diffusion coefficients in it (at a temperature of 300 K) are high, and their order of magnitude is close to that of the diffusion coefficients in liquids. This is a consequence of the high flexibility of the main chain and the weak inter-chain interaction. Thus an increase in the size of the substituent (the replacement of a methyl by a phenyl group) or the introduction of a polar substituent (the nitrile group) leads to a decrease in the diffusion and permeability coefficients. It has been suggested that the elementary act in the diffusion of the molecule of a gas in a siloxane is controlled by the cooperative movement of a section of the chain containing three monomeric silicon-containing units.[16]

In spite of the high diffusion parameters of PDMS, a serious obstacle to the use of this polymer as a material for gas-separation membranes is its low selectivity with respect to many gases, and also its poor mechanical and film-forming properties. Various methods are used to overcome these disadvantages: the introduction of fillers, cross-linking, block copolymerisation, and the deposition of thin layers of PDMS on polymer supports. For example, the first gas-separation membranes were prepared from filled PDMS on a fabric support.[17] Cross-linked siloxanes are used to obtain composite membranes with a polysulphone support.[18] Non-cross-linked PDMS can be deposited on polymer supports to suppress defects or to produce thin layers with high gas-transport parameters.[19] Copolymers containing siloxane blocks will be examined in detail in section IV.

2. Vitreous Polymers

At temperatures below the vitrification temperature, the segmental mobility in a polymer disappears. From this it might have been expected that vitreous polymers would have a small free volume, and hence lower diffusion and permeability coefficients than rubbers. Since the temperature dependence of the diffusion and permeability coefficients is described by Arrhenius equations with $E_D > 0$ and $E_p > 0$, decrease in temperature leads to a decrease in P and D. In most cases, a break is observed on the Arrhenius relationships, that is the values of E_D and E_p change on passing through T_g.[6,7] At the same time, the view, which has been accepted for many years, that polymeric glasses always have lower diffusion and permeability coefficients than highly elastic polymers is not correct. In recent year, many vitreous polymers with higher diffusion and permeability coefficients than most rubbers and amorphous–crystalline polymers with low vitrification temperatures have been studied. This and other characteristics of mass transfer and sorption in vitreous polymers can be explained using the model of double sorption.[20]

Studies of the thermodynamics of sorption in a large number of vitreous polymers (see for example the paper by Paul[20] and the references therein) indicate that the sorption isotherms have the form shown in Fig.3, and are described by the equation:

$$C = k_D p + C'_H bp/(1 + bp) \qquad (6)$$

where C is the solubility, expressed in cm^3 gas (at normal temperature and pressure) per cm^3 polymer, and p the pressure, atm. The first term corresponds to the Henry isotherm (k_D is the solubility

coefficient), and the second to the Langmuir isotherm; b is the adsorption equilibrium constant, and C'_H is the adsorption capacity for the "Langmuir" fraction of the sorbed molecules. It should be borne in mind that the adsorption being considered takes place not at the gas–polymer interface but in the regions of lower density in the bulk of the vitreous polymer, that is in the elements of the non-equilibrium free volume.

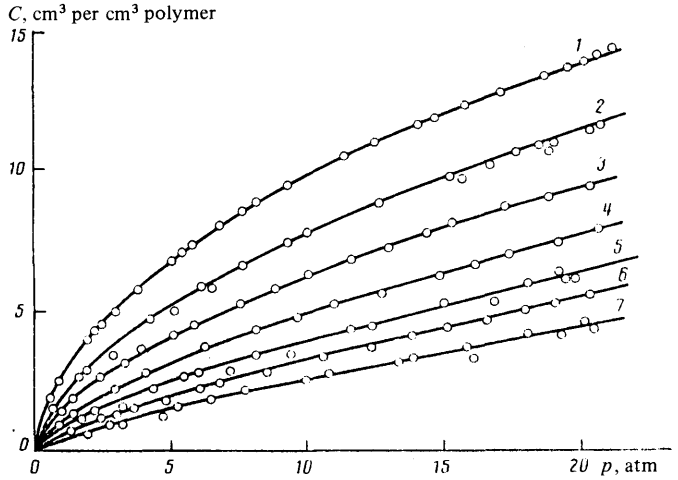


Figure 3. Sorption isotherms for carbon dioxide in polyethylene–terephthalate[21] at different temperatures K: *1*) 298, *2*) 308, *3*) 318, *4*) 328, *5*) 338, *6*) 348, *7*) 358.

The lower the temperature (in the vitreous range), the more convex the sorption isotherm towards the ordinate (see Fig.3). Since the quantity C'_H is determined as the intercept cut off on the ordinate by the asymptote approached by the sorption isotherm at high pressures (its equation is $C = C'_H + k_D p$), it follows that as T_m decreases or as the vitreous polymer moves away from its T_g, the values of C'_H increase. With increase in temperature, the curves become less convex, and at $T_m \geqslant T_g$ the isotherms become linear.

Thus the Henry isotherm describes physical solution in the polymer at temperatures both higher and lower than T_g; the second term is characteristic only of the vitreous state. At low pressures, the effective solubility coefficient is $\sigma = k_D + C'_H b$, and for highly elastic polymers, $\sigma = k_D$. This explains why the solubility coefficients are higher in polymeric glasses than in rubbers.[22] With increase in temperature, the value of σ decreases, not only because $\partial k_D/\partial T < 0$ and $\partial b/\partial T < 0$; there is a simultaneous decrease in the adsorption capacity C'_H, which reaches zero at T_g (Fig.4).

It is considered[20] that the quantity C'_H is a measure of the integral non-equilibrium free volume, which increases as the temperature $T_m < T_g$ moves into the low-temperature range. A number of data support this view. The value of C'_H at different temperatures can be determined not only from sorption data, but also from dilatometric curves.[23] This independent estimate, assuming that the density of the adsorbed gas is close to the density of its liquid phase, leads to very good agreement with the values of C'_H calculated from the sorption isotherms[21] (Fig.4).

Solution of the diffusion equation, including the two diffusion coefficients D_D and D_H for the physically dissolved and "Langmuir" fractions of the sorbate molecules respectively,[24] leads to the following expression for the observed diffusion coefficient of the gas D:

$$D = D_D \frac{1 + C'_H b/k_D}{1 + D_H C_H b/D_D k_D} \qquad (7)$$

It can readily be seen that with increase in C'_H or as the vitreous polymer moves away from its T_g, the diffusion coefficients of the gases should increase. With increase in T_g, as noted above, the diffusion coefficients of gases in polymers do in fact increase[5] (see Fig.1). This effect is evidently related to the characteristics of the thermodynamic state of polymers having high glass temperatures, since increase in T_g is accompanied by an increase in the rotational mobility of substances with low molecular weights (spin and electrochromic probes).[5] The increase in the non-equilibrium free volume in vitreous polymers whose glass temperatures are sufficiently high is also indicated by data obtained by positron annihilation[15] (Fig.2). The correlation between the activation energy of diffusion and T_g also indicates that the fraction of the free volume in polymers increases with increase in T_g.[25]

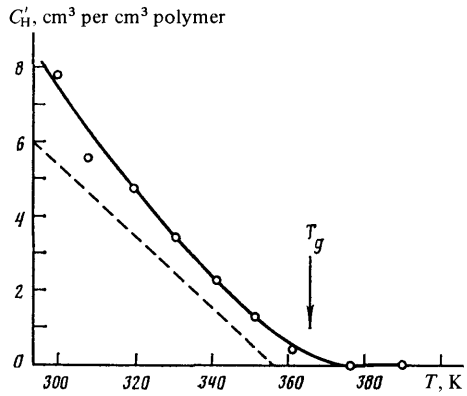


Figure 4. Temperature dependence of C'_H (for CO_2) in polyethylene–terephthalate.[21]

There arises the question of how universal are the thermodynamic relationships obtained from the model of double sorption for vitreous polymers. What is the range of change in the non-equilibrium free volume or the values of C'_H equivalent to it for different polymers? Answers to the last question are provided by the published[26] dependence of C'_H on T_g (at constant temperature) for different polymers (Fig.5). In spite of the marked differences in the chemical character of the polymers examined and the wide range of glass tem peratures, the value of C'_H is determined only by the extent to which the polymer has moved from its glass temperature. The relationshi shown in Fig.5 also applies for other sorbates (for example SO_2 [27]).

Thus the high diffusion and permeability coefficients of polymers with high glass temperatures are due to the appreciable magnitude o the non-equilibrium free volume. Physically, this means that a vitreous polymer at room temperature has the same free volume as some highly elastic polymer at a much higher temperature. The increase in the non-equilibrium free volume with decrease in the

temperature T_m in the range below T_g, that is with increase in the difference $\Delta T = T_g - T_m$, is apparently related to the fact that the decrease in the amplitude of the small-scale movements at lower values of T_m and large differences ΔT leads to the appearance in the vitreous matrix of an additional free volume, which is greater, the larger ΔT.[21,28]

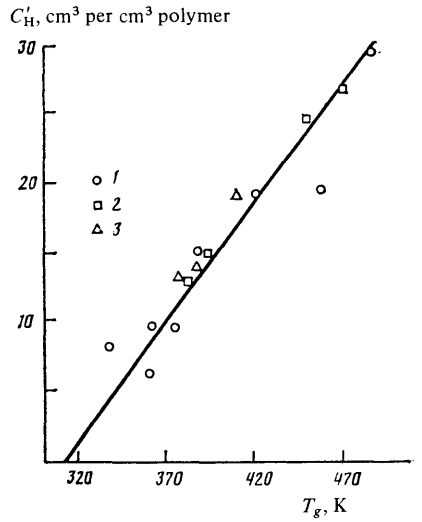


Figure 5. Correlation between the parameter C'_H for the sorption of CO_2 at 308 K and the glass temperature of polymer:[26] *1*) homopolymers, *2*) copolymers of polyphenylene oxide and polystyrene, *3*) copolymers of a polycarbonate and a polyester.

It has been suggested[29] that in the free volume, the fractions f_T and f_v corresponding to the thermal motion and the non-equilibrium character of the polymer respectively should be distinguished. Since f_T and f_v should be expected to change in opposite ways on moving away from T_g, it follows from the equation

$$D = \alpha \exp\left[-\beta(f_T + f_v)\right] \qquad (8)$$

which comes from the theory of free volume, that extremal relationships may appear, for example with change in T_g by plasticising the glassy polymer. Relationships of this type have in fact been obtained for the translational and rotational mobility of substances with low molecular weight.[29–33]

Additional confirmation of the role of small-scale mobility in diffusion phenomena observed in vitreous polymers is provided by the correlation between the frequency of rotation of the small groups of the macro-chains (from NMR data with rotation of the specimen at the "magic" angle) and the diffusion coefficients of gases (H_2, CO).[32] The extremal character of the relationships for v_f is also indicated by data obtained by using electrochromic probes to study the free volume in glassy polymers.[34] These relationships are observed when T_m does not differ greatly from T_g, that is when the contribution (f_T) of the small-scale mobility to v_f becomes appreciable against the background of f_v.

Although the model of double sorption can be used to describe the mass transfer and sorption of both individual gases and their mixtures,[35] in the great majority of glassy polymers which have been studied, the phenomenological character restricts its predictive power. It is intuitively clear that the coefficients of diffusion, permeability, and gas-separation selectivity should be determined not so much by the integral free volume (C'_H) as by the size distribution of the elements of the free volume and their distribution in space, the interaction between the substance diffusing and the polymer, and the equilibrium between the two groups of sorbate molecules (physically dissolved and adsorbed).

The model cannot give this information, so that it is desirable to study diffusion and sorption in vitreous polymers by independent methods. Thus the existence of a rapidly established equilibrium between the two groups of sorbed molecules, corresponding to the Henry and Langmuir isotherms, has been demonstrated by NMR.[36] It was recently shown that by studying the thermodynamics of sorption by reverse gas chromatography it is possible to estimate the characteristic dimensions of the elements of the non-equilibrium free volume in a polymer.[37] It was found that the more closely the geometric dimensions of the sorbate molecule correspond to the dimensions of the element of the non-equilibrium free volume, the more exothermic the mixing process and the more hindered the state of the sorbed molecules. This is revealed in large negative entropy effects.

On the other hand, attempts are being made to construct a diffusion model which takes account of the energy of the inter-chain interaction and the geometric dimensions of the molecules of the diffusing substance and the substituents of the macro-chains.[38,39] It will be shown below that the available data on the diffusion and sorption properties of vitreous polymers make it possible in some cases to relate their large free volume to definite characteristics of the structure.

III. VITREOUS POLYMERS—MATERIALS FOR GAS-SEPARATION MEMBRANES

The recent increase in interest in energy-saving and ecologically clean technologies, and progress in the chemistry and technology of the treatment of polymers, led in the nineteen-seventies and eighties to the development of several types of industrial gas-separation membranes, used in various technological processes. All gas-separation membranes used in present-day practice are based on glasssy polymers.

Just as among highly elastic polymers the greatest free volume is shown by the silicon-containing polymer PDMS, among vitreous polymers the maximum values of D and P are characteristic of polymers containing Si in side groups; polyvinyltrimethylsilane (PVTMS)[40] and polytrimethylsilylpropyne (PTMSP).[41] Both PVTMS and PTMSP are amorphous high-molecular-weight polymers with high glass temperatures (170° and >200° respectively). Both polymers are readily soluble in various organic solvents, and form strong thin films. PVTMS is used to prepare a highly efficient asymmetric membrane with a diffusion layer thickness of 0.2 to 0.3 μm,[42] widely used to separate gases. The diffusion and permeability coefficients of these polymers with respect to various gases and, for comparison, the corresponding data for PDMS are given in Table 1.

It is considered that polymers in the highly elastic state are characterised by higher values of P and D than polymeric glasses. The data given in Table 2 refute these ideas. The diffusion and permeability coefficients in PVTMS are fairly high, although they are lower than the values of P and D in highly elastic PDMS. At the same time, the values of P and D for vitreous PTMSP are greater by an order of magnitude than those for PDMS.

Table 1. Permeability coefficients of organosilicon polymers and the diffusion coefficients of various gases in them.

Polymer	$10^9 P$, $cm^3.cm/cm^2.s.cmHg$				$10^7 D$, $cm^2 s^{-1}$			
	H_2	CH_4	O_2	N_2	H_2	CH_4	O_2	N_2
PDMS	65	95	60	28	430	130	160	150
PVTMS	20	1.3	4.3	1.1	180	1.8	7.6	3.6
PTMSP	700	400	400	200	—	227*	358*	255*

*Data given by Y.Ichiraku, S.A.Stern, and T.Nakagawa, J.Membrane Sci., 1987, **34**, 5.

Table 2. Permeability of the products of the polycondensation of 4,4'-hexafluoroisopropylidenediphthalic anhydride with various diamines.[44]

Diamine	$10^9 P$, $cm^3.cm/cm^2.s.cmHg$		α_{H_2/CH_4}
	H_2	CH_4	
3,5-Diaminobenzoic acid	3.4	0.012	275
1,5-Naphthylenediamine	7.8	0.072	109
1,3-Phenylenediamine	3.6	0.013	270

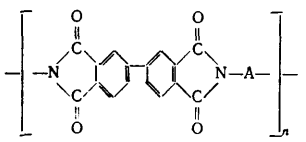
In glassy silicon-containing polymers with trimethylsilyl substituents, the appreciable free volume is probably due to the non-equilibrium state of the polymer, the large inter-chain distances, and the existence of local cavities close to the bulky substituent. This is confirmed by the relatively low density of these glassy polymers, by the results obtained by the spin probe method,[43] and by data on the thermodynamics of sorption.[37] An interesting feature is that the replacement of one methyl group by a linear alkyl group in the $Si(CH_3)_3$ groups of both glassy polymers leads to an appreciable decrease in the permeability coefficients. The long-chain alkyl group apparently fills the cavities present in the polymer, decreasing the free volume.

High diffusion coefficients are also characteristic of other polymers with bulky (non-planar) substituents: poly-4-methylpent-1-ene (PMP), poly-N-isopropylacrylamide, etc. The presence of these groups leads to relatively loose packing of the chains and to the presence of regularly arranged elements of the free volume. In particular, PMP shows an interesting characteristic: in contrast to other partly crystalline polyalkenes, its crystalline phase is characterised by an anomalously low density, lower than that of the amorphous phase. As a result, mass transfer in this polymer takes place not only through the amorphous phase but also through the crystalline phase.

Another group of vitreous polymers with high diffusion coefficients is formed by rigid-chain glassy polymers with rings in the main chain: polysulphone, polyphenylene oxide, polyimides, and cellulose acetate. The high diffusion parameters of these polymers are apparently due to weak inter-chain interactions and to steric hindrance, which prevents close packing.

The use of an aromatic polysulphone has made it possible to achieve the most impressive success in the field of industrial membrane gas-separation: the production of an asymmetric composite hollow fibre,[19] which is now used by the firm of Monsanto (USA) in apparatus for separating the gas mixtures H_2/N_2, H_2/CH_4, etc. The total number of assemblies of this kind throughout the world is much greater than 100. The coefficients of permeability and diffusion of gases in the polysulphone are lower by at least 1–2 orders of magnitude than those in the most permeable vitreous polymers, but with the thickness of the diffusion layer in the hollow fibre of ~ 0.1 μm this ensures a sufficiently high permeability with respect to hydrogen (30 litre $m^{-2} h^{-1} atm^{-1}$) with sufficiently high separation factors, for example $\alpha_{H_2/CH_4} = 37$ and $\alpha_{H_2/CO} = 23$.[19] The selectivity of the asymmetric hollow fibres, however, is only slightly lower than that of continuous films of the polysulphone, because of the thin protective covering, which "heals" defects.

Polyimides, that is the products of the polycondensation of aromatic diamines and dianhydrides, give a very high selectivity of separation of many gas mixtures. A simple and important example is provided by the polyimides obtained from the anhydride of biphenyltetracarboxylic acid:



where A is an aromatic residue. The chemical structure of polymers of this class can be varied considerably by introducing different units joining the aromatic rings, but most polymers retain high gas-transport parameters (Table 2).

The firm of Ube Industries (Japan) uses polyimides with the above structure to produce gas-separation membranes in the form of an asymmetric hollow fibre (trade mark Upilex).[45] These membranes can be used at temperatures up to 150° and pressure drops up to 140 atm, and give a separation factor of 200–250 for H_2/CH_4 mixtures.

Not only synthetic but also natural polymers can be used as material for membranes. The best examples are the cellulose esters (acetate, nitrate, ethylcellulose). The influence of hydrogen bonding decreases with increase in the degree of esterification of the cellulose. Cellulose acetate is used to produce asymmetric membranes with thin working layers with a thickness of ~ 0.1 μm,[46] used in the gas-separation equipment of the reel type which the firm of Separex (USA) offers for separating CO_2/CH_4 mixtures in the production of natural gas and in the tertiary production of petroleum. The data given below show that the gas-transport parameters of this polymer are comparable with those of polysulphone:

Gas	H_2	O_2	N_2	CH_4	CO_2	C_2H_6
$10^9 P$, $cm^3.cm/cm^2.s.cmHg$	0.35	0.068	0.023	0.014	2.0	0.0068

The H_2/CH_4 separation factor is equal to several tens of units.

IV. HETEROPHASE POLYMER MEMBRANES

The difficulty of producing polymer membranes having the required permeability, selectivity, and stability was noted above. Attempts are increasingly being made to solve this problem by using composite materials containing phases in the highly elastic and glassy states, and also the phases of low-molecular-weight solid and liquid additives.

A trend which is developing particularly actively is that associated with the production of various block copolymers, used as materials for separation membranes, into which a rigid vitreous block is introduced in addition to flexible siloxane components. This family of materials includes siloxane–carbonate,[47,48] siloxane–sulphone,[49] siloxane–arylate, siloxane–urethane, and other types of block copolymer.

In the selection of the components for the synthesis of block copolymers, particular attention is paid to the improvement of the mechanical properties, the chemical stability in the media being separated, or, finally, the selectivity of separation of the various components. In particular, the good mechanical properties of siloxane–carbonate block copolymers have made it possible to use them to produce ultrathin composite membranes with a diffusion layer thickness of 0.1–0.2 μm. The permeability coefficients of one of these membranes (MEM-079) are given below:[50]

Gas	N_2	CH_4	CO_2	H_2	H_2O
$10^9 P$, $cm^3.cm/cm^2.s.cmHg$	0.35	0.44	8.4	4.5	100

Improved mechanical and film-forming properties are also shown by siloxane–arylate block copolymers.[51] Their selectivity is determined by the selectivity of the siloxane component.

In siloxane–sulphone block copolymers,[49] since there are no easily hydrolysed Si–O–C bonds in the main chain, there is a sharp increase in the hydrolytic stability. In this respect, these block copolymers are much superior to siloxane–carbonate and siloxane–arylate block copolymers (Carbosil, Silar) and cross-linked siloxane polymers (Lestosil). The high chemical stability of polysulphones is also used in the production of other block copolymers (Seragel) which show a high selectivity in the separation of the mixtures SO_2/N_2, H_2S/CH_4, CO_2/CH_4, etc.[49]

Block copolymers in which not only the highly elastic but also the rigid (glassy) block has high gas-transport parameters might be of particular interest as selectively permeable polymers. This combination of properties has been realised in block copolymers containing PVTMS as the rigid block, and PDMS or polydienes (for example polybutadiene) as the soft (highly elastic) block.[52]

In polymers of this type, the permeability and diffusion coefficients of gases are highly sensitive to the composition and morphology of the copolymer. If the concentration of one of the components of the block copolymer is less than 20%, electron microscopy and analysis of the dependence of P and D on the copolymer composition show that it generally has a morphology of the "disperse phase–dispersion medium" (DPDM) type. At a concentration of one of the blocks equal to 50 ± 15%, phase inversion takes place, and the morphology is best described by a model of two interpenetrating networks. Since the siloxane phase has much higher values of P and D, a sharp increase in the integral diffusion and permeability coefficients is observed, and the overall composition dependence of these quantities is S-shaped. The proposed models of mass transfer in these systems (examined, in particular, in Ref.53) provide an insufficiently accurate description of the diffusion process over a wide range of compositions.

Attempts to refine the diffusion models encounter two fundamental difficulties. One difficulty is that the morphology of real heterophase block copolymers and polymer mixtures cannot always be reduced to simple structures of the DPDM type. Sometimes one of the components may form both a continuous and a disperse phase, and the latter is present in larger dispersion elements of the second component (an analogue of multiple emulsions).[54] Partial mixing of the chains at the phase interfaces and spatial non-uniformity of the membrane, for example enrichment of its surface in one of the components, are possible. As a result, different diffusion paths may be realised when different gases and vapours are transferred through these heterophase membranes.[53,55] This indicates the importance of the selection of the nature of the "diffusion probe" in the diffusion-structural analysis[56,57] of relatively complex systems of this type. In the analysis of uniform structures, the variable parameters may be the geometric dimensions of the different probes (cross-section, molar volume, etc.), whereas in the case of heterophase systems it is also necessary to vary the solubility parameter of the diffusing substance or its components, which influence the affinity of the diffusing substance and the separate phases of the polymer. At the same time, a new possibility is opened up for increasing the selectivity of gas separation using composite non-uniform membranes.

The second difficulty is that in the description of mass transfer in these membranes it is necessary to specify the local properties (coefficients of diffusion, solubility, etc.) of the individual phases. Since these are not known, it is assumed that these phases have the properties of the homopolymers. To verify the justification for this approach, it is appropriate to use probe methods. In particular, the spin probe method has shown that the diffusion coefficients of gases in the silane phase of silane–siloxane block copolymers coincide with the diffusion coefficnets in PVTMS.[53] At the same time, as shown by reverse gas chromatography[58] and spin probe[53] methods, the thermodynamic properties of the siloxane phase in copolymers differ considerably from those of PDMS.

The search for materials for separation membranes reduces to the search for polymers in which high values of P_i (and hence D_i or σ_i) for some gases are combined with low values of these parameters for other gases. In a large number of cases (He/N_2,[1] H_2/CH_4,[59] O_2/N_2 [3]) it has been shown that for most polymers, a single correlation applies: higher values of P_i correspond to a lower selectivity α_{ij}. An attractive method of overcoming this difficulty is by producing membranes in which transfer takes place through a phase in a different state of aggregation, for example in the liquid phase. The diffusion coefficients are usually greater by 2–3 orders of magnitude in liquids than in polymers. If the liquid phase filling the pores of the membrane shows selective solvent power for one of the components of the medium being separated, a highly permeable and selective membrane should be obtained. Quasi-liquid membranes of this type have been proposed for separating various gas mixtures. Some examples are given in Table 3. Attempts to use quasi-liquid membranes to separate CO, H_2S, and SO_2 from mixtures with other gases have been reported.[3]

In spite of the obvious advantages of membranes of this type, their use involves considerable technical difficulties: removal of solution from the pores of the membrane is possible; with increase in the gas pressure, the rate of transfer often does not increase, as in ordinary polymer membranes, but decreases; the effective thickness of the membranes is generally not less than 100–200 μm, whereas in polymer membranes it may be three orders of magnitude smaller; also the complex-forming reagents added to the solutions are often insufficiently stable.

Attempts are therefore still being made to give the membrane an increased selectivity with respect to the passage of certain gases without a significant lowering of the diffusion coefficients on transfer through the polymer phase.

Table 3. Characteristics of various quasi-liquid membranes.

Mixture	Diffusion medium	α_{ij}	$10^9 P_i$, $cm^3.cm/cm^2.s.cmHg$	Refs.
CO_2/CH_4	aqueous solutions of K_2CO_3 and Cs_2CO_3	—	—	[59]
CO_2/O_2	ditto	160	10	[60]
O_2/N_2	Co complexes in aqueous solutions	20—30	10^2	[3]
C_2H_4/C_2H_6	aqueous $AgNO_3$ solution	70—1000	10—10^2	[61]
Alkanes $(C_2—C_4)/CH_4$	n-decane, n-hexadecane	4—60	10^2—10^3	[62]

Specifically interacting additives may be present in the membrane as a solid solution. Thus the introduction of a number of inorganic salts (KF, KNO_3, etc.) into membranes based on mixtures of cellulose and polyethylene glycol leads to a selective increase in the permeability and solubility of CO_2, and also to selectivity of the separation of a CO_2/N_2 mixture with very little decrease in the effective diffusion coefficients of CO_2.[63] The porphyrin complex of cobalt(II), added to a polybutyl methacrylate matrix, increases both the permeability towards oxygen and α_{O_2/N_2}:[64,65]

Concentration of the complex, %	$10^9 P$, $cm^3.cm/cm^2.s.cmHg$	α_{O_2/N_2}
0	0,64	3,2
2,5	0,98	4,8
4,5	2,3	12,0

Many other types of complex interacting specifically with oxygen are known (Schiff bases, chelate complexes, haems with different structures, etc.), and their methods of synthesis and sorptive properties have been studied.[66]

If a complex-forming additive with an affinity for one of the components of the mixture being separated is not covalently bonded to the polymer, it may show a tendency to undergo phase segregation, as a result of which its efficiency decreases. Preference must be given to immobilisation of the additive on the macro-chain. There are at present few examples of studies in which an increase in selectivity and permeability has been observed as a result of the ionic, covalent, or other bonding of the complexes to the polymer matrix.[67—69] The search for membranes of this type for the concentration of oxygen from air and water is particularly intensive.

Extremely interesting possibilities for membrane gas separation are opened up by the use of polymer membranes containing low-molecular-weight liquid crystals, and membranes based on liquid-crystal polymers. Mixtures of polymers and liquid crystals with different structure and morphology show a higher permeability than the vitreous polymer matrix into which they are introduced.[70,71] These systems are characterised by a sharp inflection on the temperature dependence of the permeability coefficient with a few degrees of the temperature (T_m) of the crystal→liquid crystal transition. The values of P, for example for the $C_1—C_4$ hydrocarbons, increase by a factor of 100—200.[70,72,73] This increase is a consequence of the fact that at the temperature of the phase transition there is a sharp change in the solubility coefficients, but a particularly marked change in the diffusion coefficients.[74] Similar relationships were previously observed for the polyethylene—paraffin wax system;[75] an abrupt increase in the diffusion coefficients was observed in the region of the melting point of the paraffin wax.

The dependence of the permeability coefficients of C_n n-alkanes on the carbon number n is determined by the physical state of the poly-mer matrix;[22] for rubbers and partly crystalline polymers, P increases with increase in n, whereas for polymer glasses it decreases. The conversion of a system from the crystalline to the liquid-crystalline state leads to a qualitative change in the relationships, and hence in the mechanism of transfer, at temperatures below T_m, the highest permeability coefficients among $C_1—C_4$ n-alkanes are observed for methane, whereas above T_m they are observed for butane.[72—74] Thus the use of polymers containing added liquid crystals opens up the possibility of controlling not only the permeability but also the selectivity of membranes.

It is interesting, in particular, that in systems containing liquid crystals in the mesomorphic state, the separation factor α_{O_2/N_2} increases with increase in temperature.[76] This is an example, as yet rarely encountered, of a simultaneous increase in both the permeability and the selectivity.

Another possibility for improving the characteristics of a membrane separation process is by the effect of electrical and magnetic fields on the rate of mass transfer in the membranes. Thus the permeability coefficient with respect to n-butane increases by a factor of ~5 when an electric potential of ~700 V is applied to a membrane containing a liquid crystal, to bring about orientation of its molecules.[71]

The permeability and selectivity also depend significantly on the characteristics of the actual liquid-crystal state. Poly-γ-benzyl glutamate can form a smectic phase when obtained from a solution in benzene, and a cholesteric phase when obtained from a solution in methylene chloride. As a consequence of the lower density of packing in the cholesteric phase, the permeability coefficient with respect to benzene is six times greater.[77]

Liquid-crystal polymers should apparently have a number of advantages over mechanical mixtures of polymers and low-molecular weight liquid crystals. Studies in this direction have only just begun however. It has been established, in particular, that if the mesogenic groups (that is the groups giving the polymer its liquid-crystal properties) are in the main chain, the changes observed on passing through the temperature of the phase transition are more marked than when these groups are present in the side chains and lead to the formation of smectic liquid crystals.[76] The nature of the temperature dependence of the permeability of comb-shaped liquid-crystal polymers can be altered considerably by recrystallisation of the side chains.[78]

Almost all present-day membranes are obtained from familiar polymer materials, sometimes with slight modification. The directed synthesis of polymers for gas-separation membranes is as yet a rare exception. At the same time, accumulated knowledge of the chemical character and structure of polymers and their physical and phase states, and the understanding of the regularities and physicochemical principles of mass transfer in these materials are on the one hand providing a basis for the directed synthesis of polymers specially designed for separation membranes. On the other hand, these developments are opening up the possibility of producing membranes in the form of complex multifunctional structures.

The membranes which will be produced in the next ten years should reach a qualitatively new level: the range of gases being separated will increase, the permeability will increase by at least 1—2

orders of magnitude, and the quantitative single-stage extraction of the components of mixtures and operation under severe conditions will become possible.

While the present review was being prepared for publication, a number of papers confirming the role of the free volume in the sorption and transfer of gases in vitreous polymers were published. Maeda and Paul[79–81] have studied the influence of added plasticisers on the sorption, diffusion, and permeability of gases in polysulphone and polyphenylene oxide, and also the specific volumes of mixtures containing these polymers. It was shown that the free volume, determined as the difference $v_f = v - v_0$, where v is the specific volume, and v_0 the occupied or van der Waals volume, that is the specific volume at 0 K, provides and excellent description of the diffusion and permeability coefficients of gases in a wide range of plasticised and non-plasticised polymers. In some cases an appreciable increase in the selectivity of separation of gases α_{ij} can be achieved by changing the free volume.[82] Estimates of the characteristic dimensions of the elements of the non-equilibrium free volume in vitreous polymers by the spin probe method[43] and by reverse gas chromatography[37,83] have been confirmed by an independent determination using photochromic and fluorescent probes.[84] It was established that in polystyrene, the average volume of the elements is 260–280 Å^3, and that elements with dimensions greater than 400 Å^3 are not present, that is the size distribution is fairly narrow.

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The Role of Interphase Phenomena in the Processes of Ion Transport Through Liquid Membranes

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The principal interphase phenomena accompanying the transfer of a substance through liquid membranes (chemical reactions, the formation of supersaturation and microheterogeneity zones, spontaneous interphase convection), which are related to many important characteristics of the kinetics of ion transport, have been examined. By influencing these processes it is possible to control the rate of trans-boundary transfer.
The bibliography contains 61 references.

CONTENTS

I. Introduction 559
II. Chemical reactions 559
III. Supersaturation and microheterogeneity zones and condensed interphase films 561
IV. Spontaneous interphase convection 562

I. INTRODUCTION

Liquid membranes are finding increasing application for the extraction, concentration, and separation of substances of different kinds,[1,2] and also for modelling individual functions of biological cell membranes.[3-5]

A liquid membrane is a layer of an organic phase separating two aqueous solutions. This layer may be thick or extremely thin, and may be free or deposited on a solid porous material which gives the resulting system mechanical stability. A large number of emulsions of the water–oil–water type are also used. Processes using these emulsions are called membrane or emulsion extraction.[2]

Irrespective of how the membrane process is organised, a common feature is the presence of "accepting" and "delivering" phase interfaces; extraction takes place at the first of these, and re-extraction at the second. Another common feature is that the physicochemical phenomena at the boundaries of the immiscible liquids and in the extremely thin layers adjoining them, and also at the boundaries with the solid, play an extremely important and sometimes a decisive role in ion transport.

These interphase phenomena include chemical reactions, adsorption, surface association, the formation of supersaturation and microheterogeneity zones (SMZ), the formation of condensed interphase films (CIF), and spontaneous interphase convection (SIC). In thin membranes or when organic phases fixed to solid carriers are used, the formation of inverse micelles and aqueous channels becomes important. These phenomena are closely related to one another and to the processes of ion transport. A good example is provided by spontaneous interphase convection, a phenomenon whose study may give results of considerable scientific and practical importance, in particular the development of the cheapest methods of intensifying ion transport in heterogeneous systems.

The aim of the present review was to examine the principal interphase processes accompanying the transfer of substances through liquid membranes and their inter-relationships and interdependence.

II. CHEMICAL REACTIONS

The liquid phase of a membrane usually contains a carrier, that is an active component which interacts with ions to give lyophilic compounds soluble in the organic phase. The carriers may be neutralic, acidic, or basic substances, which react with the ions being extracted by ion exchange, the formation of coordination compounds, or both mechanisms simultaneously (chelate formation). In a number of cases, for example when salts of amines and quaternary ammonium bases are used as carriers, an important role is played by the formation of ion pairs (contact pairs and pairs separated by water molecules) and hydrogen bond formation. The transfer of metal ions by macrocyclic crown ethers and cryptands takes place as a result of the inclusion of the metal cation in the cavity of the macro-ring, in which it is retained, usually, by ion–dipole interaction forces. Donor–acceptor interactions and the formation of coordinate bonds may also play an important role in this case (for example in the transfer of actinide and lanthanide ions).

Thus as in the "classical" method of extraction,[6,7] in membrane methods using carriers, mass transfer is accompanied by chemical reactions, whose rate may have a significant influence on the intensity of the entire process of mass exchange. As in extraction, it is possible to distinguish processes involving the previous formation of the compound being extracted (that is a compound of the component being extracted and the carrier), the actual formation of the extractable compound, chemical transformations of the latter during its transport through the membrane, decomposition of the extractable compound at the other side of the membrane, and subsequent reactions involving its decomposition products.

Experience accumulated in the study of the kinetics of chemical reactions in extraction[7] indicates that the formation and rupture of hydrogen bonds, proton transfer, and ionic and molecular association or dissocation do not limit the rate of trans-membrane transfer, but may influence it concentration dependence by changing the individual resistances to the diffusion of each of the components in the membrane phase and in the aqueous solutions surrounding it.

The formation (and decomposition) of coordination compounds of the carriers and the components being extracted are slower, and therefore create an additional (chemical) resistance, taken into account by appropriate equations for the additivity of the phase resistances.[7] In this case, within homologous series of organic carrier reagents, as in extraction,[7] correlations may be observed between the stabilities of the compounds and the rates of trans-membrane transfer. The formation (and decomposition) of intra-complex kinetically inert compounds is even slower.[7] These reactions, which often determine the rates of extraction and re-extraction, may also limit the rate of trans-membrane transfer,[2,8] It must be borne in mind, however, that the role of the diffusion resistance of the organic phase is greater in a membrane process than in extraction, particularly in those cases where this phase is fixed on a solid support, which prevents the development of natural or forced convection.

Thus in many cases of practical importance it is necessary to take account of the rates of chemical reactions and the resistance to transfer which they create. The method used to take account of ion transport processes (the form of the equation for the additivity of the phase resistances) and, which is more important, the method used to identify these processes, depend to a significant extent on the mechanism and topology of the chemical reactions.

Chemical reactions are most frequently localised not in the entire volume or a multiphase system but only in an extremely small part of it, called the reaction zone. Exceptions are encountered only in very slow homogeneous chemical reactions, which generally are not of interest for processes of practical importance. The reaction zone coincides with the region where the main diffusion resistances are concentrated, that is with the interphase region, so that all the phenomena which alter the hydrodynamic conditions or the composition of the liquids in the interphase region should also influence the kinetics of the chemical reactions and the intensity of the mass-exchange process as a whole.[7]

One of the most obvious methods of intensifying ion transport is by increasing the rates of the chemical reactions using added catalysts. In the discussion of the mechanism of their action, two different types of interphase reactions are considered: surface and bulk (next to the surface).[7] In the transport of ions through membranes, reactions of the first type create the so-called "small merry-go-round", and those of the second type create the "large merry-go-round".[3,9] The role of the "small merry-go-round" in ion transport through a phase interface is still disputed, although the question has been widely discussed in the study of the kinetics of extraction[7] and membrane processes,[3-5,9] and has also been examined by specialists in the synthesis of organic substances in two-phase systems.[10]

The most definite conclusions reached in the study of the mechanism of formation of extractable compounds reduce to the following:[7] a surface reaction, that is a reaction involving adsorbed substances, is always accompanied by a corresponding reaction next to the surface, the contribution of the first of these being greatest at low concentrations of reagents having surface-active properties. In non-steady-state processes, the surface reaction predominates at low exposures of the phases, but subsequently the second reaction channel (the "large merry-go-round") develops, and its contribution increases.

A method has been developed for calculating the contributions of the two reaction channels,[11] and the conditions controlling each of them have been found. In particular, it has been shown for the reactions between copper ions and hydroxyoximes that extremely small quantities of added ionic surface-active substances (SAS) have a greater influence on the rates of surface reactions than on the rates of reactions localised in layers of the aqueous phase next to the surface. Anionic SAS increase the rate of both the formation and the decomposition of the copper hydroxyoximate, whereas cationic SAS decrease the rates of these reactions (see Table and Refs. 12 to 14). The acceleration factor reached 8, and the retardation factor 25, so that by using SAS it is possible to change the rate of the process by a factor of 200.[11,12]

The influence of SAS on the parameters of the extraction and re-extraction of copper in systems containing 2-hydroxy-5-octylbenzophenone oxime.[11]

SAS	c_{SAS}, M	Extraction*			Re-extraction**		
		F	P_s	P_v	F	P_s	P_v
Sodium lauryl sulphate	10^{-5}	1.1	0.38	0.62	2.1	0.40	0.60
	$5\cdot10^{-5}$	1.5	0.45	0.55	3.6	0.43	0.57
	10^{-4}	2.5	0.63	0.37	4.5	0.58	0.42
	$5\cdot10^{-4}$	4.3	0.88	0.12	7.2	0.69	0.31
	10^{-3}	4.8	0.91	0.09	8.2	0.74	0.26
Cetyltrimethyl-ammonium bromide	10^{-5}	0.8	0.38	0.62	0.4	0.32	0.68
	$2\cdot10^{-5}$	0.63	0.21	0.79	0.3	0.32	0.68
	$5\cdot10^{-5}$	0.52	0.15	0.85	0.2	0.25	0.75
	$5\cdot10^{-4}$	0.13	0.10	0.90	0.05	0.20	0.80
	10^{-3}	0.11	0.07	0.93	0.04	0.11	0.89
2-(α,α-Dimethyl-benzyl)-4-methyl-6-nitrosophenol	10^{-4}	2.3	0.30	0.70	3.0	0.33	0.67
	$2\cdot10^{-4}$	4.8	0.25	0.75	3.5	0.21	0.79
	$8\cdot10^{-4}$	6.0	0.15	0.85	7.8	0.15	0.85
	$2\cdot10^{-3}$	10.0	0.09	0.91	12.0	0.17	0.83
	$5\cdot10^{-3}$	12.0	0.07	0.93	15.0	0.12	0.88

Notation: F is the acceleration factor; P_s and P_v the contributions of the surface and volume reactions respectively; and c_{SAS} the SAS concentration.

* Conditions: pH 3.0, copper concentration in the aqueous phase 0.11 M.

** Conditions: pH 2.4, copper concentration in the organic phase 0.031 M.

Two explanations of the influence of these modifying agents are of interest. The first is based on the assumption that the stages determining the rates of the chemical reactions involved in the formation or decomposition of the extractable complexes take place within the electrical double layer, in which the nature of the distribution of the potential is influenced by ionic SAS. If these stages involve intermediate positively charged complexes, it follows that anionic SAS, as a consequence of electrostatic interaction, will increase the surface concentration of these complexes, leading to an increase in the reaction rates. The opposite picture for the adsorption of cationic SAS.

The second explanation, which reduces to so-called micellar catalysis, assumes the existence of supersaturation and micro-heterogeneity zones under non-equilibrium conditions in the interphase region. Adsorption on microheterogeneous particles, and a specific distribution of the substances between the bulk and micellar phases, may lead to an appreciable change in the overall reaction rate.[15,16]

It is important to note that "catalytic" effects of identical sign (but not absolute magnitude) have been observed not only in the transport of ions through "free" interfaces but also when an organic medium fixed on a porous hydrophobic material (polyethylene, Teflon) is used.[17]

Finally, it is necessary to discuss the mechanism of action of modifying agents which do not have strong surface-active properties but which themselves are capable of extracting ions weakly but rapidly. These substances include, for example, 2-(α,α-dimethylbenzyl)-4-methyl-6-nitrosophenol (ONP). The Table shows that increase in the ONP concentration leads to an increase in the contribution of the reaction next to the surface, which becomes the predominant reaction at high ONP concentrations. The acceleration is most probably due to the appearance of an additional reaction channel in the layers next to the surface in the organic phase; when ONP is present, an exchange reaction between the *o*-nitrosophenol residue (R′) and the hydroxyoxime residue (R) begins:

$$CuR_2' + H_2R \rightleftarrows CuR_2 + H_2R'$$

The production of additional reaction channels in the aqueous and organic phases is the main reason for the increase in the rate of the transfer of cations by alkyl hydrogen phosphates[18] and tri-n-octylphosphine oxide.[19]

In organic syntheses in two-phase systems, this mechanism of the acceleration of ion transport is known as "transport catalysis".[10]

III. SUPERSATURATION AND MICROHETEROGENEITY ZONES AND CONDENSED INTERPHASE FILMS

The transport of ions through a phase interface is accompanied by the transfer of the solvent, in particular water, since dehydration is not instantaneous. It penetrates to a definite depth, depending on the ratio between the diffusion coefficients and the rate constants of dehydration.

The existence in the interphase region of hydrodynamic fluctuations which are due to the statistical nature of the turbulent pulsations produced under the influence of the mixing assemblies or as a result of the existence of Marangoni–Gibbs effects, leads to corresponding fluctuations in the depth of penetration of the reaction and the concentration fields. The local values of these concentrations may exceed the solubility limit, leading to supersaturation and the formation of microheterogeneous regions of the "water in oil" and "oil in water" type. This is associated with the phenomenon, frequently observed in extraction, of the production of a "fog", extending from the phase interface into the volume of the phases. The formation of SMZ provided a basis for the development of the concept of the "sandwich" structure of the interphase region in the transport of ions through a liquid–liquid phase interface.[7,17]

According to these ideas, the interphase region includes the adsorption layer and the adjoining supersaturated and microheterogeneous layers layers of the organic and aqueous phases, whose properties and extent depend significantly on the direction and intensity of the ion transport. The assumption that there is a dynamic interphase structure, in contrast to the static structure usually considered, has made it possible to explain successfully the electrical properties of the interfaces in various liquid–liquid systems, and also a whole series of unusual kinetic relationships (saturation of the mass fluxes through the "delivering" phase interface,[7,17,20] the extremal dependence of the rate of ion transport on the concentration of the complexes being transferred in the organic phase,[17] the loss of the sensitivity of the mass fluxes to change in the intensity of mixing,[17,20,21] etc.).

The production of SMZ next to the boundaries of liquid–liquid systems has a marked influence on the intensity of mass exchange. On the one hand, it decreases the trans-boundary mass flux as a result of the shielding of the surface and the decrease in the concentration gradients at right angles to the boundary, and on the other hand it increases the rate of extraction as a result of the production of tangential gradients in the interphase tension and the development of spontaneous interphase convection under the influence of Marangoni–Gibbs effects. It is true that this mechanism appears distinctly only at free boundaries, so long as the microheterogeneity zones do not undergo phase transformations. The latter are sometimes observed at strictly definite (critical) concentrations of the substance being extracted in the aqueous solutions[7,17,20] and are accompanied by an abrupt change in the rate of ion transport as a result of sharp changes in the rheological properties of the interphase boundaries. Thus SMZ have a definite aggregation (or kinetic) stability. When they lose this stability, they are converted into viscous CIF under some conditions, and into solid CIF under other conditions.[7,22]

An important consequence of the formation of SMZ in ion transport through liquid membranes is a change in the equilibrium conditions at the interphase boundaries and hence in the overall diffusion resistance calculated from the equation for the additivity of the phase resistances. For steady-state transport processes, these local boundary conditions remain unchanged with time, but they do not coincide with the conditions found on the basis of known distribution coefficients. For non-steady-state processes, the equilibrium boundary conditions change with time, since the composition and width of the SMZ do not remain constant, but depend on the magnitude of the trans-boundary fluxes.

If the thickness of the membrane is smaller than the width of the SMZ (the latter may reach $10^{-4}-10^{-3}$ cm),[17,22] the liquid is microheterogeneous throughout the entire thickness of the membrane. The quantity of the substance being transferred in it may then differ considerably from that calculated from data on the equilibrium for macroscopic phase volumes.

The production of SMZ is apparently the initial stage in the formation of aqueous "channels" in impregnated membranes, and is the reason for electrical breakdown in electrodialysis through extraction membranes.[23] If these conclusions are correct, one method of combatting breakdown may be by introducing into the system substances which increase the rate of dehydration of the ions.

The formation of CIF influences the rate of ion transport to an even greater extent than the formation of SMZ. This phenomenon is characteristic of ions which tend to undergo hydrolysis and hydrolytic association, so that their extraction is accompanied by the formation of "medusae" ("beards", "caps"), which bring about a marked deterioration in the separation of the emulsions into layers and decrease the efficiency of mass-exchange equipment.[7,17] The formation of CIF (gels) is the main reason for the decrease in the efficiency of ultra- and micro-filtration equipment and the non-rationality of the use of large pressure drops.[24,25] The mechanism of the production of gels in ultra- and micro-filters is of course different from that in extraction. The result is the same in both cases, however, namely a sharp increase in the diffusion resistance, and sometimes a decrease in the selectivity, so that it is necessary to find methods of combatting concentration polarisation of this type.

The regular features of the formation of CIF at the boundaries of liquid–liquid systems have been studied in detail for the ions of metals in the central part of the periodic system of the elements (Zr, Hf, Nb, Ta, Ti, Si, etc.).[22] There is no doubt that the conclusions reached can be extended to processes involving liquid membranes. The methods used to prevent the formation of CIF are more varied in this case than in filtration. A decisive role is played by the state of the ions in the aqueous solution and by the nature of the carrier,

the modifying reagents, and the organic solvents, whose selection can reduce film formation to a minimum.[22] It is also possible to control the processes of CIF formation by adding surface-active substances to the aqueous solutions, and also by applying a potential difference between the phases.[22]

IV. SPONTANEOUS INTERPHASE CONVECTION

Because of its considerable scientific and practical importance, the phenomenon of spontaneous interphase convection has recently been attracting increased interest.[26,27,32,33] The phenomenon is of fundamental importance, since it provides a source of information on the regular features of the production and development of the self-organising dissipative structures in non-equilibrium open systems[28,29] and on the mechanisms of the processes of the change from "order" to "chaos".[30] The practical importance of this phenomenon is due to the promising possibilities provided by the development of highly effective low-energy methods for intensifying mass-exchange processes. Published experimental data indicate that the breakdown of hydrodynamic stability, leading to the appearance of conductive movements in the interphase region, can increase the rate of ion transport by several orders of magnitude as a result of the breakdown of the diffusion boundary layer and the decrease in concentration polarisation.

Spontaneous interphase convection may be due both to local changes in the bulk properties of the phases in the region next to the surface and to the loss of mechanical stability by the interphase boundary as a result of local breakdown of the balance of the tangential forces acting on it. A decisive influence on the local changes in the bulk and surface properties is exerted by chemical reactions, processes of adsorption and surface association, the formation of zones of extended non-uniformity, such as SMZ and CIF, and the action of an electromagnetic field.[7,27]

Allowance for the role of each of these factors, not to mention their combinations, often encounters fundamental difficulties, since at present there are no adequate models for many processes of this type. For an adequate treatment of the phenomenon of SIC it is possible to use the methods of the thermodynamics of irreversible processes. A thermodynamic analysis makes it possible to obtain in the most general form expressions for the criteria of hydrodynamic instability and to reveal the importance of various perturbing parameters.[28,31] At the same time, the use of these criteria for a quantitative interpretation encounters serious difficulties, since it requires the experimental determination of phenomenological coefficients, and this is an incorrect aim at the existing level of knowledge of SIC.

From the viewpoint of the quantitative interpretation of the regular features of SIC and the study of its mechanisms, it is apparently preferable to use the classical hydrodynamic approach, based on the solution of the differential equations of the momentum balance together with the equations of state relating the pressure, density, and temperature, and the equations of convective heat transfer and diffusion. The role of the various interphase processes responsible for the breakdown of hydrodynamic stability is taken into account by introducing perturbations not only into the main equations but also, when necessary into the corresponding boundary conditions. The analysis of the stability involves the determination of the conditions which lead to an unlimited increase in the perturbations in relation to the coordinates and time.[31,32]

To develop methods for controlling the hydrodynamic instability, it is necessary to know the properties (bulk or surface) whose local changes lead to its appearance. An analysis of published data shows, however, that it is not always possible to distinguish clearly the contribution of these factors. At the same time there is no doubt that local breakdown of the balance of the tangential forces acting on the interphase surface has a decisive influence on the production of the SEC for processes of ion transport through liquid membranes with free boundaries. For these processes, the study of the role of capillary and surface electrical forces is of the greatest interest from the practical viewpoint.[34–38]

Capillary instability (Marangoni–Gibbs instability) is due to local fluctuations in the magnitude of the interphase tension. The physical significance of the mechanism of the production of instability in this case has been clearly demonstrated in Refs.31, 33–38, where it was shown that for a non-equilibrium distribution of the interphase tension in at least one of the phases there should be a movement leading to the appearance at the interphase surface of a friction force tending to balance the interphase tension gradient. The changes with time in the interphase tension gradients unavoidably lead to perturbations with time in the velocity field, which may either be quenched or increased with the passage of time. The last case corresponds to hydrodynamic instability.

The production of stable or unstable hydrodynamic conditions depends on the existence of a critical value of the interphase tension gradient, and when this is exceeded, the perturbations of the velocity field produced by the fluctuations in the interphase tension begin to increase with time. The critical value of the interphase tension gradient can be characterised by the so-called Marangoni critical number (Ma_{cr}). It has been shown that if $Ma < Ma_{cr}$ the perturbations of the velocity field are quenched with time, and when $Ma \geqslant Ma_{cr}$ the movement becomes unstable.[33,36]

An attempt has been made[39] to establish a quantitative correlation between the rate of interphase transfer and the Marangoni number under conditions of non-equilibrium distribution of the interphase tension. Subsequently, a rigorous theoretical foundation for the correlation obtained[40] was derived from an analysis of the kinetics of mass transfer in a thin film with a specified interphase tension drop at the mobile interphase boundary. The acceleration factor has been determined[41–43] for interphase transfer in a two-phase system formed by two plane-parallel layers of the immiscible liquids, where the fluxes of each of them had an ordered circulation structure. The circulation structures were described by solving the Navier–Stokes equations for a given tangential force at the interphase boundary. This analysis gave the dependence of the acceleration factor η on the Peclet number Pe. For small Peclet numbers, the relationship $\eta \sim Pe^2$ is fulfilled, whereas as $Pe \to \infty$, $\eta \sim Pe^{0.5}$. Since the rate of convective movement and hence the magnitude of Pe are proportional to the interphase tension gradient, the interphase transfer can be intensified by altering the interphase tension.

The existence of a tangential component of the intensity of the electric field acting on the interphase boundary leads to the product of so-called electrocapillary instability, whose regular features cannot be described without taking account of the ionic nature of the reagents being transferred through the phase interphase or adsorbed on it. A large amount of experimental data indicating the existence of an instability of this kind has been published. An example is given in Ref.44, where is was shown that the oscillator movements of an oil–water phase interface are produced only if the organic phase contains a dissolved electrolyte. This system can serve as a simple and clear example of the existence of positive and negative feedback controlling the hydrodynamic instability. The existence of this feedback is a necessary condition for the production of SIC.[28] The positive feedback is provided by the adsorption of SAS

(cetyltrimethylammonium chloride) and the negative feedback by the interphase transfer of ions.

The basic principles of the instability of this system were described in Ref.37, which examined a simple model in which the appearance of SIC was due to the action of electrostatic forces. The main result obtained in the work cited is that for ionic mass transfer between two immiscible electrolyte solutions, the hydrodynamic stability of the interphase boundary is controlled not only by the Ma number but also by an electrical factor.[37] This factor may either stabilise or destabilise the phase interface.

The search for correlations between the electrochemical and hydrodynamic parameters under conditions of hydrodynamic instability was dealt with in Ref.45. A one-to-one correspondence was established between the appearance of ordered flow, induced by ion transfer, and oscillations in the electrical voltage. In this connection, mention may be made of an extremely interesting method for visualising dissipative structures[46] in the chemisorption of carbon dioxide by aqueous solutions of amines. By using a polarisation-optical method it has been possible to record the formation of convective cells in the form of spindles with cylindrical symmetry.

The Marangoni instability produced by the adsorption of substances forming condensed interphase films at a phase interface has been studied.[47-54] The conditions were found for the production of SIC in the form of both ordered and random flow, and their characteristic parameters were determined. The experiments were carried out in a system formed by mercury and an electrolyte solution containing an added SAS, which formed a condensed interphase film.[47] In this system, third-order polarographic maxima are observed, due to the tangential movement of the interphase boundary as a result of the formation of regions with an increased interphase tension. Breakdown of the hydrodynamic stability took place only on the adsorption of substances with a high attraction constant.

A study of adsorption at a toluene–water boundary during the extraction of tetrachloropalladate anions by trioctylamine[48] made it possible to record the formation of a non-uniform CIF with the simultaneous appearance of spontaneous surface convection, produced by local changes in the interphase tension as a result of the non-uniform supply of the substance to individual regions of the interphase surface.

An extremely marked increase in the rate of mass exchange under conditions of hydrodynamic instability was recorded[49-54] in a study of SIC during the extraction of metals in systems of practical importance. An increase in the rate of ion transport by more than two orders of magnitude was observed. A large amount of experimental materials showed that the breakdown of the hydrodynamic stability of the interphase boundary and the appearance of spontaneous movements in the liquid in the interphase region always take place when the extraction process is accompanied by the formation of CIF.

A typical example is provided by the extraction of the lanthanides and various actinides from nitric acid solutions by solutions of di-2-ethylhexyl hydrogen phosphate in non-polar diluents such as octane, decane, and toluene.[7] A study of the kinetics of mass transfer in a system consisting of two layers of phases in contact in tubes with a diameter of 1–3 mm without deliberate mixing showed that extremely intensive SIC takes place for several tens of seconds after the phases are brought into contact. The coefficients of mass transfer reach values of $(5-8) \times 12^{-2}$ cm s^{-1}. The breakdown of hydrodynamic stability was due to the non-uniform formation of CIF at the interphase surface. The interphase tension gradients produced lead to an oscillator movement of the interphase boundary and to intensive movement of the liquids in the interphase region, which is gradually quenched and stops completely when the film produced forms a continuous layer covering the entire interphase surface and reaches a certain strength level. If part of the interphase film is subsequently removed, mass transfer through the renewed sections of the surface again leads to destabilisation of the interphase boundary and the appearance of intensive movements in the phases.

Spontaneous rupture of the continuous interphase film and the production of movement of the interphase boundary and the adjoining layers of liquid are frequently observed. Sometimes this process is periodic in character.[53] The production of hydrodynamic instability is influenced significantly by the concentrations of the reacting components. Critical values have been detected for the metal and extracting agent concentrations, above which mass transfer unavoidably leads to breakdown of the hydrodynamic stability of the interphase boundary and the appearance of spontaneous surface convection. The concentration ranges of the existence of SIC are fairly wide, from 10^{-1} g litre^{-1} to several tens and even hundreds of g litre^{-1} with respect to the metal concentration and from 10^{-3} M to 1–1.5 M with respect to the concentration of the extracting agent.

In these extraction systems it was experimentally established for the first time that the rate of ion transport under SIC conditions depends on the ratio of the thicknesses of the layers of the phases in contact. There exists a critical value of the ratio of the thicknesses, at which extremely high rates of mass transfer are observed.[52-54] Thus breakdown of the ratio of the thicknesses of the phases acts as another destabilising factor. This conclusion is consistent with the results of theoretical studies[35] which show that the ratio of the thicknesses of the layers of the phases in contact influences the dimensions of the range of stable states. Cine- and photo-recording in cells with a width of 1 cm has revealed the structure of the hydrodynamic fluxes in the interphase region.[53] At all ratios of the thicknesses of the layers of the phases in contact different from the critical ratio, SIC appears in the form of circlation cells. The calculated values of the Reynolds number for currents of this kind did not exceed 150. At a ratio of the layer thicknesses equal to the critical ratio, the nature of the movement of the liquid changes sharply. Intensive eruptions, penetrating to a depth of 2–3 cm into the aqueous phase, are produced. The maximum rate of movement of the liquid reaches several tens of cm s^{-1}, and the value of the Reynolds number lies in the range 200–2000. Forced mixing of the phases did not have a negative influence of the parameters of mass transfer under SIC conditions, and merely decreased slightly the time interval before it began in those cases where these conditions were not established immediately after the phases were brought into contact. Other conditions being equal, the surface of even relatively large drops with a diameter of 3–5 mm was found to have a higher hydrodynamic stability than a planar phase interface. For this reason, ion transport through a planar interphase surface was more intensive. The addition of small quantities of various SAS, for example dodecanol, initiated the production of SIC.

The above material represents the main ideas regarding the role of SIC in the transfer of substances through free interphase boundaries. The question of the role of SIC in the constrained movement of liquids and contrained diffusion in systems with non-free interphase boundaries remains open. For its solution, it is necessary to take account of the existence of long-range surface forces[55] in the analysis of the role of hydrodynamic instability in the processes of transport through impregnated liquid membranes and multiple emulsion membranes.

Published experimental data indicate that hydrodynamic instability can also lead to an appreciable intensification of ion transport in systems with non-free interphase boundaries.[56-60] Thus the passage of an alternating electric current through impregnated membranes increases the rate of ion transfer,[58,59] probably due to the appearance of convective movements in the membrane phase. The dependence of the rate of ion transport on the frequency of the alternating current is described by a curve with a maximum.[59] The authors of Ref.60 consider it more promising to use an alternating current with a frequency of 1 Hz, and they assume that a current with this frequency acts directly on the liquid–liquid interphase surface, leading to the production of tangential movement on it.

An attempt to establish the relationship between the characteristic dimensions of the pores in an impregnated membrane and the rate of transfer[61] showed that increase in the pore diameter leads to a significant increase in the effective values of the diffusion coefficients in the membrane, apparently as a result of the production of convective movements in the pores.

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Thus many characteristic features of the kinetics of ion transport through liquid membranes are related to interphase processes of different kinds. The existing views on these processes do not yet give a completely consistent picture. At the same time there is no doubt that systematic studies in this field can give results of scientific and practical importance which should lead to a deeper understanding of the regular features of ion transport and to the solution of the problems of intensifying and controlling the rates of membrane processes.

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New Trends in the Development of Polymeric Materials for Reverse Osmosis Membranes

Yu.E.Kirsh and Yu.M.Popkov

Synthetic polymeric materials used for the preparation of asymmetric and composite membranes are examined. The reactions leading to the synthesis of these polymers and ways of obtaining a thin barrier layer which determines the principal quality parameters of the membranes are described. Attention is specially concentrated on the interfacial polycondensation reaction between acid chlorides and amines in order to create a barrier layer with a high selectivity and permeability.
The bibliography includes 32 references.

CONTENTS

I. Introduction 566
II. Polymeric materials for asymmetric membranes 566
III. Polymeric materials for composite membranes 567

I. INTRODUCTION

Membranes for reverse osmosis have found most extensive application in devices and apparatus designed for the desalination of brackish waters and sea water, for the conversion of industrial waste water into high-quality fresh water, for the separation of valuable side products in the petroleum, petrochemical, chemical, electrochemical, and cellulose-paper industries, for the concentration of food products in the food industry, etc.[1-3]

Numerous papers and patents concerning the preparation of reverse osmosis membranes incorporating synthetic polymers have been published during the last 10–15 years. Despite the considerable advances made, the interest in the search for new approaches in this field has not waned. A series of unsolved problems remain in the science of membranes of the type considered. Certain difficulties still exist in the interpretation of the mechanism of the segregation of water from aqueous salt solutions. Ideas concerning the influence of the chemical structure of the polymer and the processes occurring during its synthesis, its conformational and configurational states under the conditions of the formation of the membrane, and the arrangement of the macromolecules and their associated species on the surface as well as other macromolecular characteristics on the separation of substances under the conditions of reverse osmosis have been inadequately developed.

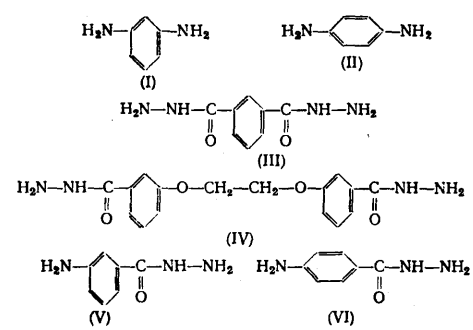
A survey of the available information about the polymeric materials used in the manufacture of the membranes can promote the development of these ideas and can stimulate the development of membranes for reverse osmosis with a high selectivity and permeability and capable of working at low pressures.

II. POLYMERIC MATERIALS FOR ASYMMETRIC MEMBRANES

Qualitatively new acetylcellulose membranes were first prepared in 1959,[2,4] which promoted a vigorous development of the application of reverse osmosis in the desalination of water. Such membranes are prepared by pouring a solution containing a water-soluble pore-forming additive over a solid surface with subsequent evaporation of the solvent at low temperature, coagulation in ice water, and annealing in hot water. Cellulose acetate containing 39.8% of acetyl groups is normally employed.[4] In this case, the membrane has an asymmetric structure, because it consists of a very thin dense surface layer, called the barrier layer, and a more porous lower layer. The molecules of the permeating solution encounters most resistance in a thin barrier layer, where they are in fact separated. However, such membranes also suffer from a series of disadvantages. The susceptibility of the acetate groups of acetylcellulose to hydrolysis in acid and alkaline solutions limits the employment of the membranes in practice and their sensitivity to microbial infection dimishes their useful life in the purification of water.

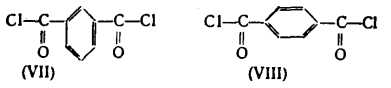
For this reason, membranes for reverse osmosis, which have a higher chemical stability than traditional acetylcellulose membranes, began to be developed since 1969. New polymeric materials distinguished by a high chemical and thermal stability have been found and new approaches have been devised to the creation of a thin barrier layer[5,6] in asymmetric and composite membranes. The latter differ from the former by the fact that their barrier layer consists of a polymeric material differing from the material of the coarsely porous base.

The first asymmetric membranes made from a non-cellulose material[5] found extensive application in the desalination of brackish waters and sea water. The modular devices for this purpose consists of hollow fibres made from aromatic polyamines or polyhydrazides. These polymers are synthesised by condensing aromatic diamines, aromatic dihydrazides, or aromatic aminohydrazides with aromatic acid chlorides in a solvent—*N*-methylpyrrolidinone (or dimethylacetamide).[5-8] *m*-Phenylenediamine (I), *p*-phenylenediamine (II), the dihydrazides (III) and (IV), for example, the dihydrazide of isophthalic acid (III), and aminohydrazides, for example, the hydrazides of *m*-aminobenzoic acid (V) and *p*-aminobenzoic acid (VI), are used as the first component:



The second component is a mixture of isophthaloyl chloride (VII)

and terephthaloyl chloride (VIII) in proportions of 7 : 3.



(VII) (VIII)

The polymers obtained are readily soluble in organic solvents. When only the acid chloride is used instead of the mixture, the resulting polymer can undergo rapid crystallisation, which hinders the preparation of the casting solution.

The casting solution for the preparation of asymmetric planar membranes can contain, for example, 15 wt.% of the polymer in dimethylacetamide with added $LiNO_3$ (35% of the weight of the polymer[5]). The film obtained on a glass plate after casting is kept in air and then placed in ice water for 1 h, after which it is washed with distilled water. The influence of the concentration and nature of the solvent and also of the nature of the salts on the formation of an asymmetric membrane has been considered.[8] The data presented in Table 1 show that the structure of the polymer influences the permeability of the membrane to water, while the selectivity remains equally high. The flux of liquid through a homogeneous film prepared from one of the aromatic polyamides [the diamine (I) and (VII/VIII) in proportions of 7 : 3] is smaller by a factor of almost 180 than that through an asymmetric membrane of the same thickness made from the same material and having the identical selectivity.[5]

Table 1. The flux of water (P) and the selectivity (S) of certain polyamide membranes.*[6]

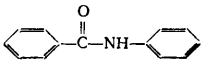
Composition of initial monomer mixture		P, litre m^{-2} h^{-1}	S, %
component 1	component 2		
(I)	(VII)/(VIII) (7:3)	8.5	99.8
(IV)/(III) (5:8)	(VII)/(VIII) (7:3)	22	99.3
(V)/(VI) (8.3:1.7)	(VII)/(VIII) (7:3)	28	99.5

*Conditions of the test: 30 °C; 3.5% NaCl solution; pressure over the membrane 10.3 MPa.

Electron microscopy of the thin barrier layer in the asymmetric polyamide-hydrazide membrane showed a closer-packed layer comprising "micelles" having a diameter of 40–60 nm. This layer consists of spherical aggregates or globular domains between which there are 7.5–10 nm cavities.[8]

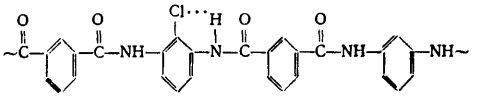
Membranes based on aromatic polyamides are manufactured in the form of hollow fibres with an external diameter of 85 μm, an internal diameter of 42 μm, and a barrier layer whose thickness ranges from 0.1 to 1 μm.[5] These membranes have a high mechanical strength, which eliminates the need for the employment of a support capable of withstanding a high pressure, and their chemical stability is also high at neutral pH.

After prolonged use of such membranes, their sensitivity to the chlorine dissolved in water was observed.[5] In order to elucidate the mechanism of the decrease in the selectivity of the membrane prepared from compounds (I), (VII), and (VIII) [for (VII)/(VIII) = 7 : 3], a study was made of the interaction of a compound modelling the material of this membrane with bromine dissolved in water.[9] Benzanilide (IX), which contains all the principal groups present in the polymer, was chosen as the model compound:



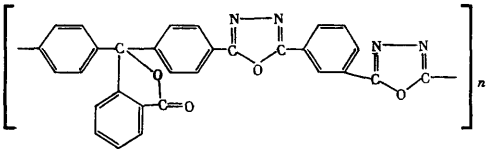
(IX)

As bromine acted on compound (IX), it gradually replaced the hydrogen in the benzene ring of the amino-component. The results obtained permitted the conclusion that, when the polymer was treated with chlorine, substitution took place in the ortho-position of the benzene ring of the diamine, i.e.



and that intramolecular hydrogen bonds between the halogen atom and the H–N group in the compound formed arose instead of the intermolecular hydrogen bonds –C=O...N–N–. Naturally such chemical changes disturb the structure of the polyamide chains and alter the submicrostructure of the polymer and hence increase the flux of liquid and reduce the selectivity of the membrane with respect to the salt. This confirms the existence of a close relation between the initial structure of the polymer, the conformation and state of the macromolecules in the aggregates, and the arrangement of the macromolecules in the barrier layer, on the one hand, and the permeability of the membrane to water and its selectivity in the reverse osmotic process, on the other.

Poly-1,3,4-oxadiazole is also used as the polymeric material for an asymmetric membrane:[10]



The membranes are obtained by casting a 20–40% solution of the polymer in methylpyrrolidinone onto a glass or metallic surface polished to a mirror finish with subsequent maintenance of the film in an atmosphere with a humidity of 80–100% for 1 h and the coagulation of the film in a precipitation bath containing water. As a result, the barrier layer is generated at the support–film boundary and not at the film–air boundary, as happens, for example, in the preparation of polyamide membranes with rock-forming additives. The membrane obtained is capable of retaining 98.5–99.2% of the salt from a 1% NaCl solution and its permeability to water is 20–25 litre m^{-2} h^{-1}.

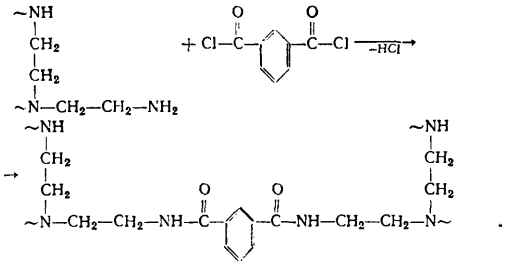
III. POLYMERIC MATERIALS FOR COMPOSITE MEMBRANES

A composite membrane for reverse osmosis consists of a thin barrier layer, a microfilter, and a base, usually a polyester base, which serves to increase the mechanical strength. Microfilters made of a polysulphone, which possesses high chemical and mechanical stability, are usually employed. Numerous investigations have been devoted to the preparation of a barrier layer,[11] from which it can be seen that the creation of this layer requires a high degree of technological sophistication and constitutes to some extent an art, scientifically well-founded criteria for the selection of the type of polymer (structure and type of functional groups) being so far lacking.

One can distinguish several principal approaches to the creation of the barrier layer. They are based on the possibility of the occurrence of the following chemical reactions on the surface of the support: (1) interfacial polycondensation between the amine and the acid chloride; (2) acid polycondensation; (3) radiation-induced cross-linking and plasma polymerisation.

1. Interfacial Polycondensation

Polyethyleneimine + aromatic acid dichlorides. In 1970 a new method was developed for the creation of the barrier layer by the interfacial polycondensation of the low-molecular-weight isophthalic acid chloride (VII) with high-molecular-weight polyethyleneimine (PEI).[11] The polysulphone support is saturated with an aqueous solution of PEI (0.5–1% solution) and is transferred to hexane containing compound (VII) (0.1–1% solution). The chemical polycondensation reaction with evolution of HCl takes place rapidly at the water–hexane interface. Since the PEI used contains primary and secondary amino-groups (the ratios of the primary, secondary, and tertiary groups are 3 : 4 : 3) and has a high molecular weight (from 10^4 to 6×10^4), interchain cross-linking of the PEI molecules takes place via the mechanism



The presence of cross-linked or branched polymer molecules at the interface between two liquids leads to the arrest of the reaction owing to the restriction of the diffusion of the amine from the aqueous phase and of the acid chloride from the organic phase. PEI which failed to react therefore remains under this layer. In order to obtain a high quality membrane, heat treatment at 110 °C, which promotes the cross-linking of the pure PEI with evolution of ammonia, is necessary.

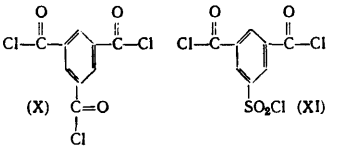
A membrane of the NS-100 type[12] consists of three layers of different porosity: the barrier layer made up of the cross-linked polyamide, the transversely cross-linked PEI layer which enters into the pores of the support, and the polysulphone microfilter. The role of the first and second layers in the creation of a high-quality membrane has been demonstrated by the following two experiments. When PEI is simply cross-linked without polycondensation, the resulting membrane has a low selectivity (70% with respect to NaCl) combined with a high water flux (92 litre m^{-2} h^{-1}).[11] If the NS-100 membrane is subjected to heat treatment at 75 °C and not at 110 °C, its selectivity falls from 99 to 96%.

Although the NS-100 membrane has a high salt-retaining capacity, it also suffers from a number of disadvantages: an insufficiently large water flux at a pressure of 10.3 MPa (~30 litre m^{-2} h^{-1}), a high sensitivity to chlorine, and a low mechanical strength of the upper layer.

In order to overcome these disadvantages, attempts have been made to replace PEI by other polymeric amines.

Polymeric aliphatic amines + dichlorides and trichlorides of aromatic acids. It has been suggested that compounds obtained from polyepichlorohydrin and ethylenediamine [13] and from polyepiiodohydrin and 4-(aminomethyl)piperazine [14] be used as the polymeric amines. A barrier layer more resistant to oxidation by chlorine can be obtained by condensation with compound (VII).[15]

Polymeric amines of other structures have been obtained by the reaction of amines with a polymeric anhydride, for example, by the reaction of triethyleneamine with the copolymer of maleic anhydride and methyl acrylate.[16] It has been suggested that a mixture of compound (VII) with the chloride of benzene-1,3,5-tricarboxylic acid (X) be used as the second reaction component:



After the interfacial polycondensation between the above polymeric amine and the mixture of acid chlorides, the membrane was dried at 115–120 °C. The flux at a pressure of 4.1 MPa and 25 °C was 98 litre m^{-2} h^{-1} for a 0.5% NaCl solution with a selectivity of 96.8%.

In order to alter the permeability and selectivity of the barrier layer, methods have been developed for its preparation from polyamides containing different numbers of free amino- and carboxy-groups.[17] Partly protonated or partly alkylated PEI and the chloride of benzene-1,3,5-tricarboxylic acid (X) and 3-chlorosulphonylisophthaloyl chloride (XI) were used. However, the barrier layer obtained was extremely hydrophilic and possessed a low selectivity.

Low-molecular-weight amines + dichlorides and trichlorides of aromatic acids. In order to obtain a barrier layer resistant to the prolonged action of chlorine, low-molecular-weight diamines (in particular, piperazine[18,19]) have also been used. The interaction of piperazine with compound (VII) makes it possible to produce a layer fairly resistant to chlorine and having a selectivity of 90–96% with respect to sea water. However the NS-300 membranes obtained in this way have not come to be widely used because they are inferior to the NS-100 membrane in their selectivity and permeability.

There exist interesting data concerning the influence of the composition of the mixture of compound (VII) with compound (X), interacting with piperazine, on the characteristics of the membranes for reverse osmosis.[6] The change in composition influences significantly the selectivity and permeability of the membrane relative to NaCl solution and solutions of bivalent metal salts ($MgCl_2$) (Table 2).

The conditions governing the formation of the barrier layer are as follows: the aqueous phase containing 1% of piperazine, 1% of Na_3PO_4, and 0.5% of dodecyl sulphate and the hexane phase containing 1% of the acid chlorides. The membrane obtained from a mixture of 33% of compound (X) with 67% of compound (VII) and piperazine is most effective for the separation of $MgCl_2$. It is characterised by a very high permeability combined with an extremely high degree of salt retention. The membrane obtained from 10% of compound (X) and 90% of compound (VII) possesses a high capacity for the retention of the salt from NaCl solution. The presence of free carboxy-groups in the barrier layer, formed as a result of the

hydrolysis of the residual acid chloride groups, promotes the retention of salts with bivalent ions:

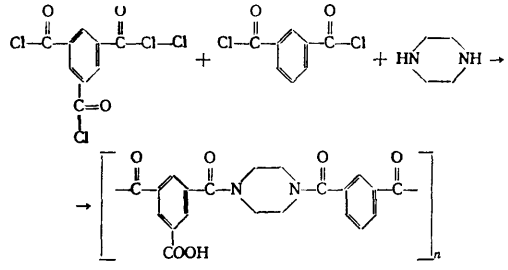


Table 2. The influence of the composition of the mixture of isophthaloyl chloride and the chloride of benzene-1,3,5-tricarboxylic acid on the properties of the membrane with respect to $MgCl_2$ and NaCl solutions.[11]

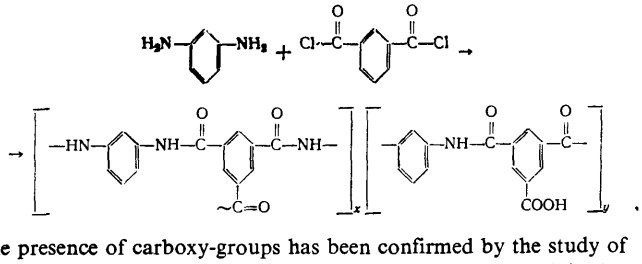
Composition, %		0.5% $MgCl_2$ solution (1.4 MPa)		3.5% NaCl solution (10.3 MPa)	
(X)	(VII)	P, litre m^{-2} h^{-1}	S, %	P, litre m^{-2} h^{-1}	S, %
100	0	43	99.3	133	68
75	25	52	99.3	160	64
33	67	128	99.9	157	65
25	75	97	99.6	121	78
10	90	30	99.9	55	96
0	100	6.7	99.0	33	98

Notation: P is the water flux and S the selectivity.

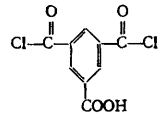
The NS-300 membranes are not manufactured on an industrial scale because of the considerable non-reproducibility of their properties.[11] The reaction of piperazine with the acid chloride is itself probably difficult to control. When piperazine is replaced by aromatic diamines, it is possible to obtain high-quality membranes for reverse osmosis.

Aromatic diamines + aromatic tricarboxylic acid chlorides. The creation in 1978 of the FT-30 membrane was a major step foward in the development of the technology for the preparation of highly efficient membranes for reverse osmosis.[20,21] The barrier layer on a polysulphone support is created in this case by the interfacial polycondensation of aromatic diamines, for example, compound (VII), with aromatic acid trichlorides, for example, compound (X). Linear chain sections, sections with branched macromolecules, and regions of cross-linked macromolecules arise during the reaction.

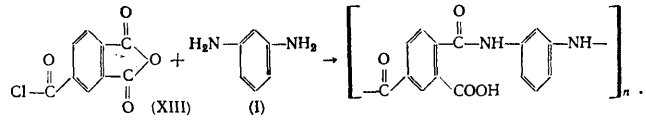
It has been demonstrated by the ESCA method that the polymer in the barrier layer contains 72% of cross-linked and branched forms (x) and 28% of linear sections with a carboxy-group (y):[22]



The presence of carboxy-groups has been confirmed by the study of the adsorption of cationic dyes. The lack of solubility in sulphuric acid indicates a cross-linked structure of the polyamide barrier layer. The presence of the cross-linked structure influences significantly the characteristics of the membranes for reverse osmosis.[11] Thus, if the barrier layer is obtained from the bifunctional acid chloride (XII)



mixed with compound (I), whereupon a cross-linked structure does not arise, then the membrane exhibits a low selectivity with respect to NaCl (from 60 to 80%). The layer obtained from the acid chloride of trimellitic anhydride (XIII) and the diamine (I) has the same characteristics:



These data indicate the existence of a definite relation between the degree of cross-linking and the morphology of the formations (aggregates) generating the barrier layer.

It has been observed by electron microscopy that the barrier layer in the FT-30 membrane consists of several layers of different density with an overall thickness of ~0.25 μm.[11] It possesses a high chemical stability and resistance to wear. The membrane can be sterilised in boiling water without change in its properties. The recommended pH range in the solutions where the membrane is sufficiently stable is between 3 and 11. The membrane can be regenerated by treatment with phosphoric and nitric acids. It is more resistant to chlorine than the NS-100 membrane, the greatest stability being observed at pH 5–6. With increase in pH, the properties of the membrane subjected to the action of dissolved chlorine are impaired. This membrane has found extensive practical application in roll-type elements and is characterised by 99.0–99.2% salt retention and a flux of 40 litre m^2 h^{-1} when a 3.5% solution is used under pressure of 5.5 MPa.

A new composite membrane for reverse osmosis, obtained by employing interfacial polycondensation, has been developed recently.[23] The barrier layer consists of a cross-linked aromatic polyamide, whose structure is close to that of the series FT-30 membrane. The membrane is characterised by an extremely high (99.5%) salt retention with respect to NaCl (0.15% solution), a high water flux (40–50 litre m^{-2} h^{-1} at 1.5 MPa), and resistance to chlorine and hydrogen peroxide.

Thus the interfacial polycondensation method gives rise to considerable possibilities for the preparation of highly efficient membranes for reverse osmosis. Presumably more efficient membranes with a high selectivity and permeability at a reduced working pressure (1–2 MPa) can be developed in this way. A low working pressure is extremely significant from the standpoint of reducing the energy consumption in the desalination process.

2. Acid Polycondensation

In order to obtain a barrier layer on the surface of the polysulphone microfilter, the acid polycondensation reaction of low-molecular-weight hydroxyl-containing compounds is used.[24,25] For

this purpose, one prepares a mixture of furyl alcohol, sulphuric acid, and a solution of polyoxyethylene (molecular weight 10^4) in proportions of 2:2:1. Polyoxyethylene is introduced in the form of a solution of 80:20 mixture of water and isopropyl alcohol. The reaction mixture is deposited on the surface of the support and dried at 125–140 °C. This results in acid polycondensation of furfuryl alcohol with formation of a polymeric barrier layer. However, after prolonged tests the membrane selectivity with respect to NaCl falls, which is associated with the irreversible swelling of the layer in the salt solution, the hydrolysis of the sulphate linkages, and oxidation (by the oxygen and chlorine dissolved in water).

When 1,3,5-tri(hydroxymethyl)isocyanuric acid (XIII) is used together with furyl alcohol for the condensation reaction, it is possible to obtain a membrane with better parameters.[25] The surface of the support is treated with a mixture of one part of compound (XIII) and two parts of furyl alcohol. The polymerisation on the surface is carried out at 150 °C. The membrane obtained is characterised by the following parameters: 99.5% salt retention with respect to NaCl (0.25% solution) and a flux of 20.5 litre m^{-2} h^{-1}. The Toray Industries (Japan) Company developed an extremely effective membrane (PEC-1000) for reverse osmosis apparently using the above condensation reaction between furyl alcohol and compound (XIII) in the presence of an acid.[26]

The cross-linking of sulphonated polysulphone on the surface of the support can also be included among the acid polycondensation reactions.[6] For this purpose, the initial polysulphone is sulphonated with chlorosulphonic acid in order to obtain a water-soluble polymer. The surface of the microfilter is coated with an aqueous solution of the polymer and is subjected to heat treatment at 100° to 140 °C, which results in the formation of a barrier layer comprising the cross-linked sulphonated polysulphone. Together with a high selectivity with respect to NaCl (98%), this membrane has a small water flux (2.5 litre m^{-2} h^{-1}). A major advantage of the membrane is its high resistance to chlorine after very prolonged action of the latter (5000) h).[27]

3. Radiation-induced Cross-linking and Plasma Polymerisation

The method consisting in the cross-linking of a surface film made up of sulphonated poly(phenylene oxide) (SPPO) by ^{60}Co γ-radiation has been applied to produce chlorine-resistant membranes with a high permeability.[8] The SPPO film is deposited on a porous polysulphone support, dried, and exposed to radiation. Best results have been obtained for doses of 2–5 Mrad; the salt retention increased from 88 to 98% and the water flux rose from 20 to 40 litre m^{-2} h^{-1}.

It has also been suggested that plasma polymerisation of vinyl and other organic compounds be used to create a barrier layer on a dry macroporous support.[29–32] However, these studies have not so far gone beyond laboratory research.

The data presented indicate the existence of a wide variety of approaches to the creation of membranes for reverse osmosis. The use of the interfacial polycondensation reaction between amines and an acid chloride is most promising. The possibility of extensive variation of the structure of both the low-molecular-weight components and of the polymers has been demonstrated in this instance. This helps in its turn to establish a relation between the structure of the polymer and the properties of the barrier layer under the conditions of reverse osmosis and hence to elucidate the mechanism of the segregation of water from aqueous salt solutions under pressure.

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Modelling Reverse Osmosis

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After a brief presentation of the principal kinetic and thermodynamic aspects of the theory of reverse osmosis, the present review examines various physicochemical mechanisms of the selectivity of membranes with respect to electrolyte solutions: the electrochemical mechanism, related to the charge of the pore surface; the dielectric exclusion of ions, due to image forces; and the structural mechanism, due to the change in the properties of water in fine hydrophilic pores. Methods for calculating the changes in the standard chemical potentials of ions on entering the membrane phase, and the effects of the Donnan exclusion of ions with allowance for the different charge of the membrane have been described. It has been concluded that it is appropriate to use charged membranes to separate electrolyte solutions at low concentrations. The problem of the transport of solutions through the fine pores of membranes has been formulated, taking account of the equilibrium distribution coefficients of the ions, their mobility, the charge of the membrane, and the phenomenon of concentration polarisation. Routes to the further development of the theory as applied to membranes of different types, different compositions, and solution concentrations have been discussed.
The bibliography contains 84 references.

CONTENTS

I.	Introduction	572
II.	Kinetic and thermodynamic aspects of the theory of reverse osmosis	572
III.	Non-equilibrium electrical surface phenomena and reverse osmosis	574
IV.	Principles of the theory of new electrokinetic phenomena and reverse osmosis	574
V.	The charge mechanism of reverse osmosis	575
VI.	The selectivity of non-charged membranes and the standard chemical potentials of ions	578
VII.	The dielectric exclusion of ions from membrane pores	578
VIII.	The hydrophilic character of membranes and reverse osmosis	580
IX.	The macrokinetic theory of reverse osmosis and the physical modelling of membranes	581
X.	A generalised mathematical model of the reverse osmosis of electrolytes	581

I. INTRODUCTION

The desalination of aqueous solutions by reverse osmosis is finding increasing practical application because of the much smaller quantity of energy required for membrane separation. This raises the question of the development of a theory of reverse-osmosis separation, which can be constructed using different mathematical and physical models of membranes and different physicochemical theories of the mechanism of their selectivity. The present review examines the effect on the selectivity of membranes of the charge on the pore surface, the dielectric and Donnan exclusion of ions from the membrane phase, and the structural changes in water in fine pores.

A distinguishing feature of the approach developed here is that it takes account of the influence of the fields of long-range surface forces on the equilibrium and on the transport of the solutions in membranes. As shown below, the main predictions which follow from the theoretical examination of the reverse osmosis of electrolyte solutions are confirmed experimentally.

II. KINETIC AND THERMODYNAMIC ASPECTS OF THE THEORY OF REVERSE OSMOSIS

In the reverse-osmosis desalination of solutions, the liquid which has passed through the membrane contains less dissolved substance than the liquid entering the membrane. The ability of a membrane to separate a substance is characterised quantitatively by its selectivity

$$\varphi = 1 - (c_2/c_0) \qquad (1)$$

where c_0 and c_2 are the concentrations of the salt in the original solution and beyond the membrane respectively. In the present review, for simplicity, only a binary uni–univalent electrolyte will be examined.

The excess of the salt in front of the membrane is removed continuously by the tangential flow of liquid, which ensures a steady-state process. Since the solvent passes through the membrane, whereas the salt is retained to some extent, its concentration directly at the front surface of the membrane, that is on the high-pressure side, is higher than its concentration in the incoming stream. The diffusion boundary layer produced in this way in front of the membrane is usually called the concentration polarisation layer.

The quantity of salt retained by the membrane in unit time is given by the difference $vc_0 - vc_2$, where v is the linear velocity of the liquid. This excess of salt is removed from the membrane surface by the diffusion flux, which is directed in the opposite direction to the convective flow and which can be expressed in terms of the thickness of the diffusion layer:

$$vc_0 - vc_2 = -D_e \operatorname{grad} c|_{x=0} \sim D_e \frac{c_0 - c_1}{\delta} \qquad (2)$$

where $D_e = (D^+ + D^-)/2$ is the effective diffusion coefficient of the ions in the free solution, and c_1 is the concentration of the salt at the front surface of the membrane. The description of the external-diffusion kinetics in reverse osmosis has been the subject of a large number of studies (see Ref.1); it reduces to the solution of the equation for convective diffusion with the boundary condition (2), which can be expressed in terms of the membrane selectivity, usually

assumed to be given. The concentration polarisation is also usually assumed to be known in the examination of internal-diffusion kinetics.

In the description of the steady-state process of reverse osmosis, it will be assumed that the applied pressure difference and the flux of the liquid Q are given, that there is no transfer of charge through the membrane ($I = 0$), and that the quantities Q,I, and the salt flux J_s are the same in all sections of the membrane. Since the transport of the salt is purely convective in the free solution beyond the membrane,[2-4] this leads to the important boundary condition:

$$c_2 = c|_{x=h} = J_s/2Q \qquad (3)$$

where h is the thickness of the dividing layer of the membrane. This condition makes it possible to express the unknown quantity c_2, which cannot be calculated directly, in terms of the other quantity J_s, which is also unknown but which can be calculated. For this purpose, the membrane model must be specified.

Reverse osmosis results from the difference between the kinetic and equilibrium properties of the solution in the pores of membrane and in the bulk. Different workers have related the decrease in the salt flux through the membrane to the decrease within the membrane in either the velocity or the concentration of the ions. This distinction, which is sometimes encountered in the literature, is unjustified, since the principal role may be played by either factor, depending on the properties of the membrane.

Ion transport in biological membranes[5] and concentrated dispersions (pastes)[6] has been more extensively studied than reverse osmosis. Reverse-osmosis membranes occupy an intermediate position between biological membranes and the systems which are the traditional objects of study in colloid science. Reverse-osmosis membranes with very fine pores are closer to biological membranes, and those with relatively large pores are closer to traditional colloid-chemical systems.

One of the difficulties of modelling reverse-osmosis processes is due to the wide variety of processes influencing demineralisation. Frequently, however, it is possible to distinguish the process predominating for given pore dimensions.

When reverse-osmosis membranes with very fine pores are used, a factor which also appears in biological membranes becomes important, namely the commensurability of the dimensions of the hydrated ion and the pore (the ion channel in biological membranes). A hydrated ion cannot penetrate into a pore with sufficiently small dimensions,[7] and this predetermines the ideal semi-permeability of the membrane. The difference between the observed selectivity and the maximum possible selectivity is probably due to the presence in the membrane of pores with different dimensions. If the dimensions of the hydrated ion are smaller than but close to those of the pore, the rate of flow of the liquid in the pore containing the ion is lowered. Since for a moderate salt concentration a large fraction of the pores do not contain ions, the average rate of ordered movement of the ions of the salt may be appreciably lower than the average rate of flow of the liquid.

In real membranes, the pores have a variable cross-section. As a result, both the pore dimensions and the molecular forces of the interaction of the ion with the pore walls change along its path. These changes can be described by regarding them as a series of energy barriers and potential wells. Here, the Eyring method for describing ion transport, widely used in the examination of biological membranes,[5] may prove useful. For membranes whose pore dimensions are commensurate with those of the hydrated ions, kinetic factors also become important; in this case there may be considerable deviations from equilibrium.[8,9]

Decrease in the pore dimensions leads to an increase in the selectivity of the membranes, but at the same time their efficiency decreases. It is therefore appropriate to decrease the thickness of the dividing layer of the membrane while at the same time increasing its porosity. This trend in the technology of reverse osmosis in the last ten years has led to considerable progress, associated with the production of so-called composite membranes, which show simultaneously high selectivity and efficiency.[10-12] Composite membranes also have certain disadvantages, however. The technology of their production is still complex and expensive, and the actual membranes are inconvenient in use, in particular because of their high sensitivity to mechanical damage. Progress in the use of composite membranes probably depends primarily on progress in the technology of their production.

One widely used model is the homogeneous model of a membrane.[13,14] Its characteristic feature is the possibility of any ion path, whereas in the heterogeneous model it is assumed that ion transport takes place only through the pores. In the homogeneous model it is assumed that the ions can be regarded as dissolved in the membrane. Research workers have encountered considerable difficulties in validating this model.[15] The reason is that real membranes are not perfect or free from defects, and in transport processes the defects behave like pores. In this connection, some authors[16,17] have considered two possible ion transport paths in a membrane: through the pores and through homogeneous regions.

It is appropriate to divide membranes into porous and diffusion membranes.[18] The latter are quasi-homogeneous gels, through which the solvent and the dissolved substance penetrate under the influence of a concentration gradient. These membranes have a high hydrodynamic resistance, so that they must be used in the form of ultra-thin films with a thickness of 0.02—0.04 μm, fixed to porous supports.

The representation of a membrane as a heterogeneous system is much more widely encountered. Dytnerskii's capillary-filtration model of selective permeability[7] is applicable only in this representation. The familiar model of Sourirajan[19] combines the representations of flow through pores and of preferential adsorption of the dissolved substance or the solvent on the "walls" of the pore.

The increased interest in the heterogeneous model and the importance of taking account of surface forces in this model have been noted.[20-24] Sourirajan's model has also undergone changes in this direction. Previously, in this model, the lowered concentration of the ions in the pores of the membrane was explained using the Gibbs adsorption equation.[19] The limited nature of this approach is indicated by the fact that it does not take account of the pore radius, which is an extremely important parameter in reverse osmosis. In the new improved model,[24] the concentration of ions in the pore is described with allowance for surface forces, which decrease with increasing distance from the pore wall, so that the increase in its radius becomes a factor which lowers the selectivity of the membrane.

The interest in the heterogeneous model of the membrane is not accidental, since it makes it possible to explain a number of features. Firstly, the wider the pore, the more justified becomes the use of the theory of surface forces.[25] On the other hand, the narrower the pore, the lower the accuracy of this theory, and the more difficult the quantitative description of the lowered velocity of the ions. Secondly, the sharp decrease in selectivity with increase in the pore

dimensions makes the wider pores responsible for the "ion leakage" in reverse osmosis. This means that even when the average pore dimensions are commensurate with the dimensions of the hydrated ion, the selectivity due to the presence of a certain proportion of wider pores is still important.

This justifies the particular attention paid in the present work to selectivity mechanisms which operate at pore dimensions appreciably greater than the dimensions of the hydrated ion.

Different levels of the theoretical description of reverse osmosis exist, corresponding to different degrees of detail in the model. At the most descriptive level, the given quantities are the kinetic coefficients characterising the membrane as a whole. In this case, the parameters of reverse-osmosis desalination are found as functions of these coefficients.[25-28] The kinetic coefficients characterising the membrane as a whole are in turn determined by the geometric structure of the membrane, the local values of the concentrations, and the local kinetic characteristics of the solution (such as the viscosity and diffusion coefficients of the components). The specification of these last quantities as parameters of the model and the formulation of the problem of reverse osmosis on this basis move the theoretical description to the next level. The problem of calculating the equilibrium local concentrations in the capillaries of the membrane at the molecular level is now being solved[29] on the basis of the method developed by Yukhnovskii.[30] As far as the more complex problem of calculating the local values of the kinetic coefficients in the membrane at the molecular level is concerned, only the first steps are being taken in this direction, and these coefficients still have to be specified as parameters of the model.

The above two approaches to the theory of reverse osmosis were first combined in Refs.2 and 23. The results obtained are of only limited value, however, since account was taken of only one selectivity mechanism influencing the concentration of ions in the membrane, namely the charge mechanism. Soviet scientists have recently developed a complex approach in the theory of reverse osmosis, with allowance for a variety of mechanisms. This has been the result of systematic studies of surface forces[25] and non-equilibrium electrical surface phenomana[31-33]—a new direction in colloid science.

III. NON-EQUILIBRIUM ELECTRICAL SURFACE PHENOMENA AND REVERSE OSMOSIS

As early as 1947, Deryagin[34] pointed out that the involvement of the electrical double layer in convective ion fluxes should lead (by analogy with the flow potential) to a decrease in the concentration of the dissolved substance between the ends of the capillary. The effect described was detected much later, and was subsequently called reverse osmosis. If this effect is analogous to the flow potential, there should also exist a phenomenon analogous to electro-osmosis, namely slippage in the diffuse atmosphere of the ions or molecules under the influence of the concentration gradient. In Ref.34 the existence of this effect, called capillary osmosis, was justified rigorously on the basis of thermodynamic considerations, but the conclusions applied to the case of a non-electrolyte, that is a diffuse structure of the adsorption layer of the molecules was assumed. The theory of capillary osmosis in electrolytes was developed later using the methods of the thermodynamics of irreversible processes.[35,36]

Osmosis, however, that is the flow of a substance through an ideal selective membrane under the influence of a concentration gradient, can be completely balanced by applying a pressure equal in magnitude to the osmotic pressure. As a result, the flow stops, and the system moves into a state of thermodynamic equilibrium. This constitutes a qualitative difference between osmosis and flow through an ideal membrane, that is capillary osmosis, and this is emphasised by the difference in the names. Thus osmosis is simply a limiting case of capillary osmosis, when the selectivity of the membrane tends to unity. Strictly speaking, non-ideal selective membranes are used for desalination, and it is more correct to call the corresponding process reverse capillary osmosis, and not reverse osmosis.

IV. PRINCIPLES OF THE THEORY OF NEW ELECTROKINETIC PHENOMENA AND REVERSE OSMOSIS

In the examination of reverse osmosis in membranes with relatively wide pores, it is possible to introduce the concept of the convective flow of ions, that is the entrainment of the ions by the flow of liquid. In addition, it is also necessary to take into account the diffusion of the ions relative to the liquid, brought about by the difference between the concentrations of the ions in front of and behind the membrane. This effect, which lowers the selectivity of the membrane, cannot be eliminated completely, but its negative influence can be lowered considerably by increasing the rate of flow to such an extent that the following condition is satisfied:

$$\mathrm{Pe}=vh/D_{\bullet}\gg 1 \tag{4}$$

The Peclet number Pe can be used to estimate the ratio of the intensities of the convective and diffusion fluxes. When $\mathrm{Pe}\ll 1$, diffusion makes it possible to practically equalise the difference in concentrations at the capillary inlet and outlet. When $\mathrm{Pe}\gg 1$, on the other hand, diffusion is suppressed by the strong convective flux, and the selectivity of the membrane approaches its limiting value. The basic law of conservation of the number of ions under steady-state conditions is given by

$$\operatorname{div} j^{\pm}=0 \tag{5}$$

applied to the one-dimensional problem of flow through a membrane in the form

$$\partial j^{\pm}/\partial x=0 \tag{6}$$

where $j^{\pm}$ represents the densities of the fluxes of the cations and the anions. The main difference between the diffusion-electrical theory of electrokinetic phenomena[31,32] and the classical theory of Smolukhovskii lies in the fact that it shows that it is necessary to use not a single overall law of charge conservation but the laws of conservation for the cations and anions separately. In the diffusion-electrical theory, the expression for the density of the ion fluxes is written taking account of three transport mechanisms: convection, diffusion, and electromigration:

$$j^{\pm}=c^{\pm}(x)\,v-D^{\pm}\frac{\mathrm{d}\,c^{\pm}}{\mathrm{d}\,x}\mp D^{\pm}\frac{F}{RT}c^{\pm}(x)\frac{\partial\psi}{\partial x} \tag{7}$$

where c represents the concentrations, and $D^{\pm}$ the diffusion coefficients, of the cations and the anions, ψ is the electric potential, F the Faraday number, R the universal gas constant, T the absolute temperature, and the distance x is measured in the direction of the flow of the liquid through the membrane. The expression for the ion fluxes in the macrokinetic theory of reverse osmosis is also written in this form.[2-4] Finally, for the production of a steady-state flow potential $\Delta\psi$, the condition $I = 0$ must be satisfied.

Later[3,4] and earlier[2] studies show almost no differences from the macrokinetic viewpoint. The examination of the action of surface forces in Refs.3, 4, and 32, however, raises the theory of reverse osmosis to a qualitatively new level. The authors of Ref.2 took account of a single mechanism for the decrease in the concentration of the ions close to the surface, namely the charge mechanism, due to the presence of the electrical double layer. In Refs.3, 4, 37, and 38, the macrokinetic theory was given a much more general character as a result of the inclusion of the energy of the effective interaction of the ion (or molecule) U with the pore surface. This energy is obviously a function of the distance from the ion to the surface, that is a function of r in the model of a cylindrical capillary (r is the distance to the axis of the capillary). In particular, the dependence of U on r can characterise the energy of electrostatic interaction, so that the theoretical considerations put forward in the pioneering work[2] can be regarded as a particular case of the general theory developed in Refs.3, 4, 37, and 38.

The considerable mathematical difficulties associated with the theory of the non-equilibrium electrical double layer and hence non-equilibrium electrical surface phenomena have been overcome[31,32] by using the principle of local equilibrium and by examining the conditions under which it is possible to neglect the deviations from local equilibrium. The theory of reverse osmosis was developed similarly in Refs.2 and 37–39 for the model of a cylindrical pore. The same approximation has also been extended to surface forces of any character acting on the ions in the pore.[3]

For each transverse cross-section at a sufficient distance from the ends of the capillary, it can be assumed approximately that the distributions of the concentration $C_i(x,r)$ and the energy $U_i(x,r)$ for an ion of the ith kind will be the same as if each section of the capillary were in equilibrium with an electrolyte volume characterised by definite parameters of the thermodynamic equilibrium, different for different sections of the capillary, namely the values of the concentrations of its components $c_i(x)$, the electrostatic potential $\psi(x)$, and the pressure $p(x)$. These parameters should naturally have values intermediate between the corresponding values for the solution on the two sides of the capillary.

Eqns.(7) and (5) for the ion fluxes can be supplemented by the Stokes equation

$$-\operatorname{grad} p-\sum_i C_i \operatorname{grad} U_i+\eta\Delta v=0 \tag{8}$$

where p is the hydrostatic pressure in the capillary, η the viscosity of the liquid, and Δ the Laplace operator.

Inside the capillary, where the force field of its walls is effective, the potential of the average force $f_i(r)$ is variable. As a result, its changes also alter the concentrations of the components of the solution $C_i(r)$ and the pressure $P(r)$. The corresponding distributions can be represented as the sums of their values in the uniform solution c_i and p and the changes Δc_i and π due to the influence of the walls:[3]

$$U_i=\psi+f_i;\quad C_i=c_i+\Delta c_i;\quad P=p+\pi \tag{9}$$

It can be assumed that in a cross-section at a sufficient distance from the ends of the capillary, f_i, Δc_i, and π depend only on r, and not on x. In each cross-section, local equilibrium is preserved, that is the radial fluxes are equal to zero:

$$j_r=0;\quad v_r=0 \tag{10}$$

Integrating Eqns.(7) and (8) with allowance for Eqns.(9) and (10) and using the boundary conditions for $x = 0$, which corresponds to the free electrolyte solution, where

$$f_i=0;\quad c_i=c_0;\quad \pi=0 \tag{11}$$

gives

$$C_i(x,r)=c_i(x)\exp\left(-\frac{f_i}{kT}\right);$$
$$\pi=kT\Sigma\,\Delta c_i=kTc_i(x)\sum_i\left[\exp\left(-\frac{f_i(x,r)}{kT}\right)-1\right] \tag{12}$$

where k is the Boltzmann constant.

After substituting Eqns.(12) in Eqns.(7) and (8), the latter can be represented as linear combinations of the gradients of the parameters of the thermodynamic equilibrium along the direction x:

$$Q=k_{11}\left(-\frac{\mathrm{d}p_0}{\mathrm{d}x}\right)+k_{12}\left(-kT\frac{\mathrm{d}\ln c}{\mathrm{d}x}\right)+k_{13}\left(-\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \tag{13}$$

$$J_S=k_{21}\left(-\frac{\mathrm{d}p_0}{\mathrm{d}x}\right)+k_{22}\left(-kT\frac{\mathrm{d}\ln c}{\mathrm{d}x}\right)+k_{23}\left(-\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \tag{14}$$

$$I=k_{31}\left(-\frac{\mathrm{d}p_0}{\mathrm{d}x}\right)+k_{32}\left(-kT\frac{\mathrm{d}\ln c}{\mathrm{d}x}\right)+k_{33}\left(-\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \tag{15}$$

The coefficients k_{ik} represent integrals whose calculation in accordance with Eqns.(12) requires a knowledge of the concentrations $C_i(x,r)$ in the capillary for equilibrium with a volume solution with concentration $c(x)$. Using the Onsager principle, $k_{21} = k_{12}$, $k_{32} = k_{23}$, and $k_{31} = k_{13}$.

V. THE CHARGE MECHANISM OF REVERSE OSMOSIS

1. Donnan Exclusion of the Ions

The system of equations (13)–(15) was first proposed in Ref.39 for the particular model in which the concentration of the ions in the capillary differs from the bulk concentration only as a consequence of the charged state of the capillary walls, and the potential of the average force is equal to the product of the charge of the ion z_i and the electrostatic potential: $U_i = z_i\psi$. This corresponds to the assumption that the solution in the capillary forms a diffuse electrical double layer, described in the Gouy–Chapman theory by the equation

$$\Delta\Psi=\varkappa^2\operatorname{sh}\Psi, \tag{16}$$

where $\Psi = e\psi/kT$, and the Debye length is given by the expression:

$$\varkappa^{-1}=\left(\frac{\varepsilon kT}{4\pi e^2 c}\right)^{1/2} \tag{17}$$

where e is the charge of the electron, and ε the dielectric constant.

The system of equations (13)–(15) together with the boundary conditions (3) and (11) was solved in Ref.2 using a number of simplifications, which are discussed in Ref.3. In particular, the distribution $\Psi(r)$ for each cross-section of the capillary of radius a was selected to satisfy the boundary condition:

$$\Psi|_{r=a}=\Psi(c_0) \tag{18}$$

This assumption is justified in two limiting cases, when

$$\varkappa a\gg 1 \tag{19}$$

$$\varkappa a\ll 1 \tag{20}$$

When Eqn.(19) applies, the solution of the electrolyte with a composition different from the bulk composition occupies only a small

region of the capillary next to the wall. Thus $c(x)$ differs little from c_0, and the selectivity of the membrane is correspondingly low. When Eqn.(20) applies, the potential $\psi(r)$ and hence f_i change little in the transverse cross-section of the capillary. In this case, however, ψ is almost the same for all cross-sections of the capillary, so that the simplification (18) is justified.

In Ref.3, the system of equations (13)–(15) was solved over a wide range of values of κa both with the boundary condition (18) and assuming that the charge density on the capillary surface is constant:

$$\sigma_0 = -\varepsilon \frac{d\Psi}{dr}\Big|_{r=a} = \text{const} \qquad (21)$$

It was found that the selection of the conditions for a constant charge or a constant potential has little influence on the selectivity, that is the indeterminancy associated with the usually insufficient knowledge of the mechanism of production of the double layer has no significant influence on the predictive power of the theory. In Ref.2, good agreement was obtained between theoretical and experimental data on the dependence of the selectivity on various parameters (the Debye radius, the Peclet number, and the surface potential).

Similar results were obtained for colloidal membranes.[40] A large amount of evidence for the decisive role of the surface charge has been obtained in the study of the selectivity of dynamic membranes formed from colloidal particles[41] and polyelectrolytes.[42] Although the desalinating action of cellulose acetate membranes is not determined by the charge mechanism, in the range of low concentrations this mechanism also makes a definite contribution to the selectivity in this case.[43] This was reflected in Ref.44, where the dependence of the selectivity of these membranes on the pH of the solution was described by an extremal curve with a minimum lying at the pH which ensured that the charge of the membrane was equal to zero. Since the contribution of the charge mechanism for symmetrical electrolytes is independent of the sign of the charge of the membrane, the selectivity when the charge is equal to zero should pass through a minimum. Thus the results obtained in Ref.44 shows fairly convincingly that the charge mechanism also operates in cellulose acetate membranes.

The possibility of using charged membranes with wide pores in reverse osmosis is indicated by the results obtained in Ref.45, where it was found that even the cellulose acetate ultra-filtration membranes UAM-100, in spite of the extremely low density of the surface charge of the cellulose acetate and the large pore dimensions, retain some selectivity up to an electrolyte concentration of 10^{-2} M, reaching a maximum selectivity $\varphi = 0.6-0.65$ at the minimum concentration studied, 10^{-4} M.

For high Peclet numbers, the electrolyte concentration remains practically constant and equal to c_0 along practically the entire thickness of the dividing layer (a rapid decrease in concentration takes place close to the boundary of the dividing layer and the wide-pore layer of the membrane), and the charge mechanism of reverse osmosis is revealed extremely clearly. In the case of high selectivity, which is of the greatest practical importance, the corresponding expression for the selectivity of the membrane acquires a simple form when condition (20) is satisfied.

There is a definite similarity between the charged dividing layer of an asymmetric reverse-osmosis membrane and the ion-exchange membrane used in electrodialysis. This membrane is not directly applicable for reverse osmosis, because of its large thickness and corresponding high hydrodynamic resistance. The main electrochemical regular features in the ion-exchange membrane–electrolyte system also apply, however, to the charged dividing layer of an asymmetric membrane.[46]

These regular features are: a) the shielding of the electric field of the ion by the charge of opposite sign at distances greater than the Debye length; b) the local electrical neutrality of the homogeneous phases at distances from the phase interface greater than the shielding length, and the integral electrical neutrality of the heterogeneous system as a whole; and c) the constant electrochemical potential within the heterogeneous system, that is the equality of the electrochemical potentials in the resin and electrolyte phases. Local electrical neutrality is understood to indicate that the algebraic sum of the charges of the ions is equal to zero within each physically infinitely small volume.[46] This definition will be used in the examination of the ratio of the concentrations of the mobile cations and anions in the ion-exchange membrane.

The matrix of ion-exchange membranes contains ionogenic groups, which on contact with the solvent dissociate to give a charge fixed by the surface.[50] The ions of an electrolyte whose sign is the opposite of the sign of the surface charge of the membrane are usually called counter-ions, and the ions with the same charge are called co-ions. The membrane phase must contain sufficient counter-ions to compensate the surface charge. These counter-ions are described as being exchange sorbed. Moreover, in accordance with the third of the above conditions (constant electrochemical potential), the membrane phase must also contain some co-ions. In other words, since the co-ions are in the electrolyte, they must also be present in the membrane, but at a different concentration. Since the membrane and the co-ions have charges of the same sign, the concentration of the latter in the membrane phase is lowered. It is also clear that the membrane should also contain counter-ions which in turn compensate the charge of the co-ions present. These co-ions and counter-ions are usually described as the non-exchange sorbed electrolyte. It follows that the concentration of non-exchange sorbed electrolyte in the membrane phase is lower than the concentration of the equilibrium solution. This phenomenon is called Donnan exclusion of the electrolyte from the ion-exchange membrane phase.[46–48]

In accordance with the electrical neutrality condition, the exchange sorbed counter-ions cannot leave the membrane phase, since they compensate the surface charge. Only the non-exchange sorbed electrolyte can leave the membrane; the filtrate is therefore desalinated relative to the solution being separated.

The concentration of co-ions in the membrane is lower, the larger the Donnan electric potential jump Ψ_D.[46,48] This equilibrium potential jump is produced as a consequence of the removal of some of the counter-ions from the membrane layer next to the surface into the electrolyte, as a result of which a volume charge is produced in the electrolyte layer next to the surface due to the excess of counter-ions; a volume charge of opposite sign is produced simultaneously in the membrane layer next to the surface Some of the counter-ions leave the membrane, since their concentration in the highly charged membrane is higher than that in the surrounding electrolyte. The lowered concentration of co-ions in the membrane is described in terms of the Donnan potential using the familiar Boltzmann equation.

The Donnan potential is greater, the greater the exchange capacity or the corresponding concentration of surface charges in the volume of the membrane c_f and the lower the electrolyte concentration. These qualitative relationships are confirmed by a quantitative

analysis, which leads, on the basis of a quantitative examination of the third and fourth conditions, to an expression which describes the Donnan potential and hence, using the Boltzmann equation, the concentration of co-ions in the membrane:[46–48]

$$c^{co} = \frac{1}{2}[(c_f^3 + 4c_0^3)^{1/3} - c_f] \quad (22)$$

In the case of low electrolyte concentrations, which is of the greatest interest, when

$$c_0 \ll c_f \quad (23)$$

this equation is simplified to:

$$c^{co} \simeq c_0^3/c_f \quad (24)$$

This leads to the following expression for the selectivity:

$$\varphi = \left(1 - \frac{c^{co}}{c_0}\right) = \left(1 - \frac{c_0}{c_f}\right) \quad (25)$$

from which it follows that the selectivity may approach 1 with decrease in the electrolyte concentration, when condition (23) begins to be satisfied.

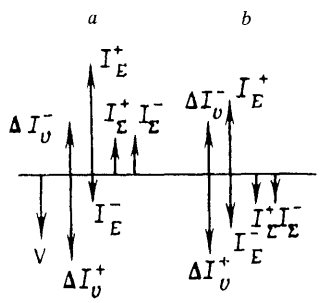


Figure 1. Influence of the transport numbers of the ions on the selectivity of the membrane.

Eqn.(25) can give a value of the selectivity which is too high, since it does not take account of the fact that the polarisation field, at the same time as retarding the counter-ions, increases the transport of co-ions through the membrane. If it is assumed that the membrane is negatively charged, the convective flux of counter-ions I_v^+ will be greater, and that of the negative ions I_v^- will be less, than if the liquid passed through a capillary, preserving the original concentration, when $I_{v0}^+ = I_{v0}^-$. In Fig.1, the corresponding arrows show the magnitude and direction of the excess convective fluxes $\Delta I_v^\pm = I_v^\pm - I_{v0}^\pm$. The distance between the ends of the arrows for ΔI_v^+ and ΔI_v^- gives the magnitude of the electric current due to the convective flux of the ions (the so-called flow current). The arrows $I_E^\pm$ characterise the ion fluxes produced under the influence of the polarisation electric field. The condition that the electric current through the membrane be equal to zero is satisfied if the distance between the ends of the arrows ΔI_v^+ and ΔI_v^- is equal to the distance between the ends of the arrows I_E^+ and I_E^-. The resulting excess fluxes of the cations I_Σ^+ and anions I_Σ^- are the same, and equal to the excess flux of the salt.

Desalination takes place when the excess flux of the salt and the flow of liquid take place in opposite directions. Fig.1*a* shows that this situation obtains if

$$I_E^+/I_E^- = a_E^+/a_E^- > \Delta I_v^+/\Delta I_v^- \quad (26)$$

where $a_E^\pm$ represents the so-called transport numbers, defining the fraction of the total current carried by the cations and the anions respectively when a potential difference is applied to the membrane in the absence of other thermodynamic forces. If the opposite inequality is satisfied (Fig.1*b*), filtration through the membrane leads to concentration of the salt. The passage of the counter-ions close to the fixed charges of the membrane may be retarded by electrostatic forces of attraction, so that $a_E^- > a_E^+$. If the fixed charges are hydrated, the distance of closest approach increases, and the electro-static attraction becomes weaker, so that the hydrophilic character of the membrane helps to satisfy condition (26).

Information on other studies of the charge mechanism is given in a detailed review.[44] The data given more or less agree with the above conclusions.

2. Asymmetric Charged Membranes as a Basis for the Creation of a Technology for the Desalination of Slightly Mineralised Water Using Low-Pressure Reverse Osmosis

The extensive introduction of reverse osmosis is being retarded, firstly, by the complexity of the equipment, and, secondly, by the low intensity of the mass exchange processes.[1,7] The first difficulty is to a large extent due to the need to use high pressures, which is unavoidable in the demineralisation of salt water, since in this case it is necessary to overcome a high difference in osmotic pressure.

In the demineralisation of brackish water, however, and in particular in desalination technology, the osmotic pressure drop is much smaller. For the requirements of power engineering and the electronics industry and for the demineralisation of brackish water, it is possible in principle to create a technology of reverse osmosis using moderate pressures. The equipment for reverse osmosis at pressures of ~10 atm is much simpler. When the membranes of the MGA series used at present are employed, however, an appreciable decrease in pressure would lead to an unacceptably large decrease in efficiency. It is appropriate to use these and similar membranes, which retain the required selectivity at high salt concentrations (as a result of the very small pore dimensions), for the demineralisation of salt water. Their use to treat weakly mineralised water is not the optimum technological solution, however. Up to the present, the synthesis of membranes has been aimed at ensuring the optimum geometric characteristics (pore dimensions, porosity, thickness of the active layer), and insufficient attention has been paid to colloid–electrochemical methods for intensifying selective membrane transport. Neglect of the role of the membrane charge is probably justified in the technology of the demineralisation of salt water. With decrease in the salt concentration, however, the conditions for demineralisation by reverse osmosis change radically.

The technology of the low-pressure reverse osmosis of slightly mineralised water should be based on asymmetric relatively wide-pore membranes with the optimum charge.

The reverse-osmosis membranes used at present are very weakly charged.[49–53] The idea that the introduction into the membrane matrix of a fixed surface charge might make the active layer looser

(as a result of the electrostatic repulsion of the charges on the surface of the pores) and hence make the membrane more efficient while preserving its high selectivity as a result of the long-range action of the electrostatic forces was first put forward in Ref.54. Since then, about a dozen papers have described attempts to synthesise and study the properties of charged reverse-osmosis membranes. The most interesting studies are those described in Refs.55 and 56. The first describes a method for obtaining membranes by sulphonating or aminating a polystyrene–butadiene resin. These membranes had a fairly high selectivity (95–98%) at low concentrations, but their efficiency was low (0.1–5 litre m^{-2} d^{-1} $atom^{-1}$) due to the large thickness of the membrane (500 μm) and its symmetrical structure. It might be possible to use this method to synthesise much thinner membranes with a high efficiency.

Another method for obtaining highly efficient membranes[56] involves the deposition and subsequent grafting of a thin layer of a polyelectrolyte on the surface of an ultra-filtration membrane. This method has been used to obtain thin-layer composite membranes with a very high efficiency (30–150 litre m^{-2} d^{-1} atm^{-1}). The selectivity was low, however (60% with respect to singly-charged anions). The authors of Refs.55 and 56 (and of other similar studies, for example Refs.57 and 58) apparently did not conclude that the most appropriate field of application of charged membranes is with fairly dilute solutions. The lack of understanding of the fact that the average concentration of co-ions along the cross-section of the pores in charged membranes can be lowered considerably has prevented a full evaluation of the advantages of charged reverse-osmosis membranes, so that work devoted to their development and study is still fairly fragmentary. Systematic work on the synthesis, study, and use in desalination of asymmetric charged membranes is therefore necessary.

VI. THE SELECTIVITY OF NON-CHARGED MEMBRANES AND THE STANDARD CHEMICAL POTENTIALS OF IONS

The lowered concentration of a salt in non-charged membranes leads to a decrease in the value of the standard chemical potential (SCP) of the ion in the pores of the membrane, due to the interaction of the ion with the polymeric dielectric matrix of the membrane or to the change in the structure of water in it.[59] A quantitative characteristic of this effect is provided by the distribution coefficient, that is the ratio of the average concentrations of the ions in the membrane phase c_m and in the bulk of the electrolyte:

$$\gamma = \bar{c}_m / c_0 \tag{27}$$

This characteristic, which is extremely important for reverse osmosis, is readily expressed in terms of the SCP, taking into account the condition for electrochemical equilibrium in the membrane–electrolyte system for both the cations and the anions, $\mu_e^{\pm} = \mu_m^{\pm}$, where $\mu_e^{\pm}$ and $\mu_m^{\pm}$ are the electrochemical potentials of the ions in the electrolyte and membrane phases respectively.

When the familiar expression for the electrochemical potential of an ion in a dilute electrolyte is used, these equations acquire the form:

$$\mu_{m0}^{\pm} \pm e\psi_m + kT \ln c_m^{\pm} = \mu_{e0}^{\pm} \pm e\psi_e + kT \ln c_0^{\pm} \tag{28}$$

where $\mu_{m0}^{\pm}$ and $\mu_{e0}^{\pm}$ are the standard chemical potentials of the ions in the membrane and electrolyte phases respectively. Eliminating the interphase potential jump from these equations and making use of the condition for local electrical neutrality in the membrane and electrolyte phases gives:

$$c_m = c_0 \exp\left[\frac{\mu_{e0}^{+} - \mu_{m0}^{+} + \mu_{e0}^{-} - \mu_{m0}^{-}}{2kT}\right] \tag{29}$$

Since in the non-charged membrane the concentrations of the cations and the anions are equal, a flow potential and hence electromigration fluxes of the ions are not produced. At high Peclet numbers, the diffusion fluxes are also unimportant. This means, however, that the salt concentration in the filtrate c_2 coincides with the salt concentration in the membrane c_m. This makes it possible to make the equation for the selectivity more specific:

$$\varphi = 1 - \gamma = 1 - \exp\left[\frac{\mu_{e0}^{+} - \mu_{m0}^{+} + \mu_{e0}^{-} - \mu_{m0}^{-}}{2kT}\right] \tag{30}$$

where γ is defined by Eqn.(27).

VII. THE DIELECTRIC EXCLUSION OF IONS FROM MEMBRANE PORES

1. Image Forces

A decisive role in the mechanism of the dielectric exclusion of ions from the pores of a membrane is played by the interaction of the ion with the polarisation charges,[60–64] which are produced at the interface between media characterised by different dielectric constants (DC). Since for a single planar interface the interaction of an ion with this interface can be described formally as an interaction with a fictitious charge or image, the phenomenon being considered is usually described as the production of "image forces". These forces play an important role in many electrochemical systems.[65]

It is possible to consider first the limiting case of an isolated ion, that is to assume that the shielding length is so much greater than the characteristic pore dimensions that the shielding can be neglected. Since the DC of the membrane matrix ε_m is lower than the DC of the solvent ε, the sign of the polarisation charges on the surface of the pores coincides with the sign of the charge on the ion. The repulsion between like charges leads to an increase in the SCP of the ion, which in accordance with the condition of constant electrochemical potentials leads to a decrease in the electrolyte concentration in the pores.

In the case of a charged membrane, only the concentration of the co-ions is lowered, and the concentration of the counter-ions is increased, whereas in the pores of a non-charged dielectric membrane the concentrations of both the cations and the anions are lowered (the concept of co-ion and counter-ion in this case is obviously meaningless); in the case of a binary symmetrical electrolyte, their excess SCP are approximately equal.

From the obvious fact that the rate of flow of the liquid and the concentration of the electrolyte have maximum values in the central part of the pore, it follows that the main contribution to the salt flux is made in this region. The results of calculations for the case of a flat capillary[66] confirm this qualitative conclusion and show that the salt flux can be estimated with a relative uncertainty of not more than 20–30%, from a knowledge of only the concentration in the central part of the pore.

The dependence of the intensity of dielectric exclusion on the geometry of the pore space is of considerable interest. When there is no shielding in the system, there is only one characteristic length, namely the pore dimensions. By changing to dimensionless

coordinates in the equations, it can be shown that in all cases the excess SCP due to the image forces W is inversely proportional to the pore dimensions. Moreover, it is always directly proportional to the square of the charge of the ion $q = ez$ and inversely proportional to the DC of the solvent. Thus irrespective of the shape of the pore, it is possible in the expression for the excess SCP of the ion to distinguish the factor $2W\varepsilon R/q^2$, and the remaining factor depends on the ratio of the DC of the matrix to that of the solvent, $\beta = \varepsilon_m/\varepsilon$.

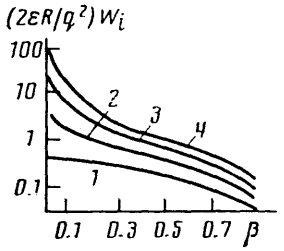


Figure 2. Dependence of the intensity of the dielectric exclusion on the geometry of the pore space:[64] *1*) ion close to a plane, *2*) planar gap, *3*) cylinder, *4*) sphere.

Fig.2 gives the dependence of $2W\varepsilon R/q^2$ on the parameter β for four cases, where the ion is situated: 1) at a distance R from a planar interface, 2) in the middle of a planar gap with a width of $2R$, 3) on the axis of a cylindrical capillary with a radius R, and 4) at the centre of a spherical cavity with a radius R.[64] A noteworthy feature is the very strong dependence of the intensity of dielectric exclusion on the geometry of the system, particularly at low values of β.

The physical significance of this dependence is that, as is well known, the density of the energy of the electric field is inversely proportional to the DC of the medium. It is for this reason that the standard chemical potential of an ion increases close to bodies with a lower DC. When a medium shows dielectric non-uniformity, the lines of force of the electric field are deformed. In this connection, the extent to which the geometry of the pore space is closed is very important; this determines the possibility that the lines of force of the field "by-pass" the regions with lower DC. For example, in the case of a single planar interface there is an entire half-space with an increased DC. In this case the energy of the "image forces" is low. At the same time, for the limiting closed geometry of a sphere, all the lines of force penetrate the medium with the low DC, so that the magnitude of W is a maximum in this case.

A spherical pore is of interest only as an example of limiting closed geometry, since flow of a liquid is impossible in it. It may be noted that the curves corresponding to the geometries of a sphere and a cylinder lie not far from one another (Fig.2), and the intensity of dielectric exclusion is also fairly high in the latter case. For example, the selectivity of a cylindrical capillary with a diameter of 3 nm ($\varepsilon_m = 3$, $\varepsilon = 80$) is ~ 0.9. Decrease in the pore dimensions evidently leads to a sharp increase in the selectivity. Thus in the case of the dielectric exclusion mechanism, membranes with cylindrical pores should "function" most effectively.

The dielectric exclusion of ions in real membranes can be reduced approximately to the solution of the electrostatic problem of an ion in a right cylindrical capillary. The membrane selectivity due to this mechanism is high, even if the pore size is much greater than the size of the ion.

The interaction of the separated ion with the polarisation charges is complicated by the presence of other ions in the pore. In the pore, each ion is surrounded by an atmosphere of counter-ions, as in the free solution. If the Debye radius is smaller than the pore radius, then the electric field of an ion situated at the centre of the pore does not in practice reach the pore surface and does not polarise it, so that the image forces are weak. A quantitative theory of this effect of shielding of the image forces has been developed using the model of a flat capillary. In this case it is possible to obtain a very simple approximate equation for the excess SCP of an ion situated on the axis of the capillary:[67,68]

$$W = \frac{-q^2}{2\varepsilon R} \ln [1 - \alpha \exp(-2\varkappa_i R)] \qquad (31)$$

where

$$\alpha = (\varepsilon - \varepsilon_m)/(\varepsilon + \varepsilon_m);$$

and $\varkappa_i^{-1}$ is the shielding length inside the pores.

Since as already noted in the case of dielectric exclusion the concentration of the ions of both signs in the pores is lowered, the "internal" shielding length is greater than the "external" length (that is the shielding length in the bulk of the equilibrium solution). Thus an increase in the selectivity of the membrane in this case leads to a decrease in the shielding effect, whereas an increase in the density of the fixed charge of ion-exchange membranes, which is accompanied by an increase in their selectivity, leads to the opposite effect.

Another interesting characteristic of Eqn.(31) is that when $\alpha < 1$, the decrease in the magnitude of W begins not at $\varkappa_i R \simeq 1$ but at $\varkappa_i R \simeq 0.2$. This is due to the fact that in the absence of shielding a large contribution to the SCP of the ion is made by so-called "multiple images". In other words, this phenomenon can be described as mutual polarisation of the surfaces; as a result, the polarisation charge as it were extends along the surface to distances which are much greater than the width of the capillary. The shielding of the interactions with it therefore naturally begins at $\varkappa_i R < 1$.

Fig.3 shows the theoretically calculated concentration dependence of the excess SCP of ions situated in flat capillaries with different widths.[68] It can be seen that the smaller the width of the pores of the membrane, the higher the concentration at which the decrease in selectivity begins. This corresponds completely with what has been said above. It should be noted, however, that even in the case of highly selective membranes, the decrease in selectivity takes place at concentrations which are not very high. This conclusion does not fully agree with experiment. Here, it is helpful to introduce the concept of non-local dielectric shielding in polar media,[69-71] which takes account of the fact that dipole shielding, like ion shielding, is fully developed only at distances greater than the correlation length (for ion shielding this is the Debye length). For water, these distances have been estimated[69] as 0.5–0.7 nm, that is they are commensurate with the dimensions of fine pores.

Strictly speaking, the interaction of an ion with polarisation charges is influenced not only by ionic shielding but also by dielectric shielding. In the local approach used up to the present, this feature is taken into account by dividing the quantity W by the static DC of the solvent. If account is taken of the non-local character of the dielectric response, it may be concluded that the DC

close to the ion is effectively lowered (since at small distances the bound charge cannot be completely formed); the interaction with the polarisation charges separated on the surface therefore increases. This leads, firstly, to a considerable intensification of the dielectric exclusion, and, secondly, to a change in the ratio of the relative contributions of single and multiple images in the excess SCP of the ions in favour of the former. The explanation for this is that the correlation length cannot be much larger than the pore dimensions; thus only the interaction with the first images experiences weak dielectric shielding, and the interaction with the other images takes place in practically the same way as in a medium with a static DC. In this situation, ionic shielding as far as $\kappa_i R \simeq 1$ should lead to a decrease in the already small contribution of the multiple images, and a significant decrease in the intensity of dielectric exclusion begins at $\kappa_i R \gtrsim 1$.

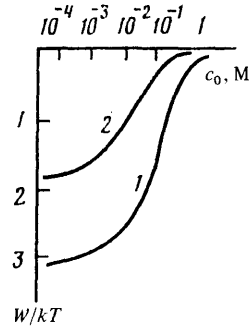


Figure 3. Concentration dependence of the SCP of ions for a model of membranes with a pore half-width of 0.3 nm (*1*) and 0.5 nm (*2*).[68]

2. The Combined Effect of the Dielectric and Charge Mechanisms

In moderately wide charged pores, the simultaneous operation of the charge and dielectric mechanisms leads to a decrease in the concentration of co-ions. If it is assumed that these effects are additive, the distribution coefficient of the co-ions is given by the equation:

$$\gamma = \frac{c^+}{c_0} = \exp\left[\frac{-e\psi + W}{kT}\right] \qquad (32)$$

The equation used to find the Donnan potential now contains the SCP, which depends on the image forces:

$$\operatorname{sh}\frac{e\psi}{kT} = \frac{c_f}{2c_0}\exp(W/kT) \qquad (33)$$

Simplifying this equation for the case of greatest interest, that of high values of the Donnan potential and substituting the result in Eqn.(32) gives

$$\gamma = \frac{c_0}{c_f}\cdot\exp(-2W/kT) \qquad (34)$$

and it can be seen that in this case there is not simple multiplication of the Donnan and dielectric factors but a quadratic increase in the intensity of dielectric exclusion.

Increase in the fixed charge, however, leads to an increase in the concentration of counter-ions, so that the shielding influence is increased. As a result, the effects of dielectric exclusion in the case of highly charged ion-exchange membranes apparently are not very significant. Membranes having a moderate charge are more promising for the combination of the effects of these two mechanisms. This leads to the practical conclusion that it is appropriate to give membranes a surface charge not only for desalination but also for the demineralisation of so-called brackish water with a higher concentration.

VIII. THE HYDROPHILIC CHARACTER OF MEMBRANES AND REVERSE OSMOSIS

In addition to the electrochemical mechanisms examined above (the Donnan and dielectric exclusion of ions), another factor leading to a decrease in the concentration of the dissolved substance in sufficiently fine pores of membranes is the change in the structure of water.[72,73] This is confirmed by the fact that hydrophilic reverse osmosis membranes effectively retard not only an electrolyte but also the neutral molecules of substances such as sugar, alcohol, and acetone.

The change in the solvent power of the pore water of hydrophilic membranes with respect to ions is due to a number of factors.[59,74] One of the results of the change in the structure of water is a lowering of its dielectric constant. The intrinsic energy of an ion in the membrane pores, calculated, for example, by the Born method, is then found to be higher than that in the free solution,[75] leading to a decrease in the concentration of the ions in the membrane pores. The Born approximation may be inadequate, however, since the mechanism of the phenomenon being considered may in fact be much more complex.[76,77]

Since there is no theoretical justification for the influence of the hydrophilic character of membranes on their selectivity, the results of some recent experiments are of particular interest. The experiments were carried out using three membranes of different hydrophilic character.[78] The most hydrophilic was a composite polyamide membrane (*A*), obtained by interphase polycondensation.[79] The other two reverse-osmosis membranes were prepared from homopolymers based on polyhydroxydiazole (*B*) and the even more hydrophobic polycarbonate (*C*). For this series of membranes, the selectivity coefficients were measured for alkali metal chloride solutions with different concentrations c_0. The highest selectivity was observed for the most hydrophilic membrane *A* (Fig.4).

The preservation of a high selectivity over a wide range of electrolyte solution concentrations (as far as 0.5–1 M) is a distinguishing feature of hydrophilic membranes. Nevertheless, their selectivity decreases with increase in the concentration of the solutions. This is due to the breakdown of the characteristic structure of water in the fine pores and the gradual approach of the structure of the solution to that in the bulk. The breakdown takes place as a result of the influence of the ions on the structure of water, which increases with increasing concentration of the solution; this increasing influence suppresses and then exceeds the influence of the hydrophilic surface of the pores.

It is natural to expect that ions which have a stronger influence on the structure of water should bring about a greater decrease in the selectivity with change in concentration. Thus Li^+ ions, which have the smallest radius and the highest hydration numbers, in all cases (Fig.4) bring about a sharper decrease in the selectivity

coefficient. On the other hand, Cs^+ ions, which have the largest radius and small hydration numbers, have less influence on the structure of water in the pores, leading to preservation of the high selectivity of the membrane and its weaker dependence on the concentration of the solution.

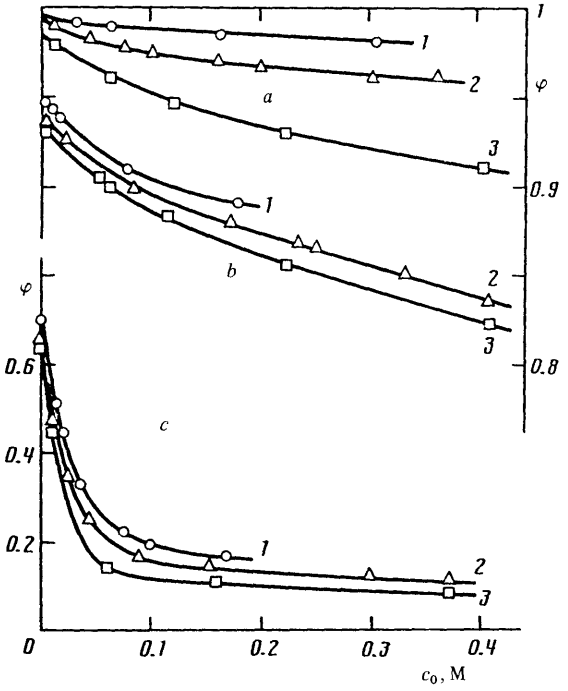


Figure 4. Dependence of the selectivity coefficient φ on the concentration of solutions of the electrolytes CsCl (*1*), KCl and NaCl (*2*), and LiCl (*3*) for membranes with different hydrophilic character.[78]

IX. THE MACROKINETIC THEORY OF REVERSE OSMOSIS AND THE PHYSICAL MODELLING OF MEMBRANES

It can be seen from the foregoing that calculations at the molecular level at present make it possible to determine only the equilibrium distributions of the components in the pores of a membrane. Even in this case, however, a purely theoretical approach to specific membranes is impossible, since, firstly, the size distribution of the pores is unknown, and, secondly, it is impossible to take account of the change in the structure of water, a factor which cannot yet be calculated quantitatively.

This makes it necessary to carry out a range of experimental measurements and compare the results with the results of a calculation of the kinetic coefficients using the system of equations of macrokinetic theory. A system of equations of this kind[80] has been used to develop a set of required measurements. The general formulation of the problem, given in section IV, was simplied in Ref.80 by introducing the boundary condition (20). This made it possible to calculate the kinetic coefficients and to obtain equations for the selectivity φ and the flow potential $\Delta\psi$:

$$\varphi = 1 - \frac{\exp(\mathrm{Pe}/k_1)}{1 - k_2 + k_2 \cdot \exp(\mathrm{Pe}/k_1)} \tag{35}$$

$$\Delta\psi = FR_m\bar{c}_0 Q - \frac{RT}{F}(a_E^+ - a_E^-)\frac{\bar{c}_s}{2c_0} \tag{36}$$

where

$$\frac{\mathrm{Pe}}{k_1} = \frac{1}{4}\frac{F^2}{RT}\cdot\frac{[\bar{c}_s - (a_E^+ - a_E^-)\bar{c}_0]QR_m}{a_E^+ a_E^-};\quad k_2 = \left[\frac{\bar{c}_s}{2c_0} - (a_E^+ - a_E^-)\frac{\bar{c}_0}{2c_0}\right]$$

$\bar{c}_s = \bar{c}^+ + \bar{c}^-$, $\bar{c}_0 = \bar{c}^+ - \bar{c}^-$ are the average concentrations of the cations and the anions in the hydrodynamically mobile part of the pore space (with a statistical weight corresponding to the distribution of the rates in viscous flow); and R_m is the electrical resistance per unit surface area of the membrane.

To determine c_0 and c_s it is sufficient to measure the following parameters by the usual methods: 1) the selectivity coefficient φ, 2) the membrane potential difference $\Delta\psi$, 3) the resistance of the membranes R_m, and 4) the transport numbers $a_E^{\pm}$. This set of measurements can give information on two of the most important characteristics of the mechanism of reverse osmosis, namely the Donnan potential (see part 1 of section IV) and the differences in the standard chemical potentials of the ions (section V). The introduction of this set of measurements in laboratories working on the theory and technology of reverse osmosis will make it possible to check different versions of the theory of reverse osmosis. A physical model of the membrane should be constructed in each specific case; this will lead to optimisation of the conditions for reverse osmosis and indicate methods for improving the quality of membranes.

X. A GENERALISED MATHEMATICAL MODEL OF THE REVERSE OSMOSIS OF ELECTROLYTES

The most general mathematical model of the processes of reverse osmosis,[4,81] which can be regarded as a further generalisation of the conclusions in Refs.3 and 37, has recently been developed. The generalisation was achieved by taking simultaneous account of membrane transport and external-diffusion kinetics, the charge and non-charge mechanisms of the exclusion of ions from the membrane pores, and the extension of the theory to unsymmetrical electrolytes and electrolyte mixtures. This has made it possible to obtain a number of results of practical importance.

The combined description of convective diffusion within a membrane and in the concentration polarisation layer involves two dimensionless Peclet numbers, one internal [Eqn.(4)], and one external, Pe_0. When

$$\mathrm{Pe}_0 = mv\delta/D \ll 1 \tag{37}$$

(where m is the porosity of the membrane, and D the diffusion coefficient in the bulk solution), concentration polarisation does not lower the selectivity of the membrane. At low flow rates v, this condition is fulfilled, but condition (4) is not. With increase in the rate, however, condition (4) begins to be satisfied, but condition (37) is no longer satisfied. Thus the theory[4,81] predicts a maximum on the curve giving the dependence of the selectivity of the membrane on the flow rate, corresponding to optimum separation conditions (curve *1* in Fig.5). The calculations were carried out for the following conditions: $\gamma_- = 10^{-2}$, $\gamma_+ = 0.1$ (which corresponds to the preferential introduction of cations into the pores), and $2h/m\delta = 1.5$. The value of the last parameter was selected for those

conditions of mixing of the solution being separated for which, for a membrane with a porosity $m = 0.2$, the thickness of the non-mixed layer δ is approximately seven times the thickness of the dividing layer of the membrane h.

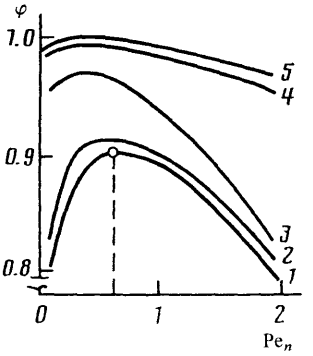


Figure 5. Dependence of the selectivity coefficient φ on the external Peclet number for different surface charges of the membrane σ: *1*) 0; *2*) 0.01; *3*) 0.1; *4*) 1; *5*) 5.[80]

From the general solutions obtained[37,38] it follows that the maximum value of the selectivity $\varphi_{max} = 1-\gamma$ is achieved for $Pe/Pe_0 \geqslant 5$. For a binary electrolyte solution

$$\gamma = \gamma_+^{z_-/z} \cdot \gamma_-^{z_+/z} \qquad (38)$$

where $z = z_+ + z_-$; z_- and z_+ are the valences of the anions and the cations.[81]

The surface charge of a membrane $\sigma = c_f/c_0$ increases its selectivity (curves *2*–*5*). For cellulose acetate membranes, the magnitude of the dimensionless charge at $c_0 = 10^{-2}$ M is $\sigma = 0.1$ (curve *3*), increasing to 1 at $c_0 = 10^{-3}$ M (curve *4*). Thus the influence of the surface charge is greater, the lower the concentration of the electrolyte solution being separated. Thus at $c_0 \geqslant 0.1$ M, the influence of the charge ($\sigma \leqslant 0.01$) is vanishingly small (curve *2*).

For an unsymmetrical electrolyte, a solution can be obtained without taking account of the influence of concentration polarisation, that is by assuming that $Pe_0 \ll 1$. Fig.6 shows the dependence of the selectivity of the membrane on the dimensionless surface charge $\Delta = \sigma/z_+z_-$ (for a 1–1 electrolyte, $\Delta = \sigma$). For $\Delta = 0$, the selectivity of the membrane was taken as equal to $\varphi_{max} = 0.9$. For the unsymmetrical electrolytes $BaCl_2$ (curves *1* and *2*) and $LaCl_3$ (curves *3* and *4*), the selectivity depends on the sign of the charge of the membrane pore surface Δ. Here, curves *1* and *3* correspond to $\Delta > 0$, and curves *2* and *4* to $\Delta < 0$. The efficiency of the retardation of the solution is much greater when the sign of the charge of the multiply-charged ion is the same as the sign of the charge of the membrane. This is because the surface charge has a stronger influence on the more highly charged ion. Thus for $BaCl_2$ and $LaCl_3$, a higher selectivity is achieved when the membrane has a positive charge. On the other hand, for the effective separation of, for example, Na_2SO_4 solutions, it is appropriate to use negatively charged membranes, in agreement with experiment.

Since the values of Δ depend on c_0, the graphs in Fig.6 also reflect the influence of the electrolyte concentration for a fixed membrane charge ($c_f = 5 \times 10^{-3}$ M). The corresponding values of $c_0 = c_f/z_+z_-\Delta$ are given on the upper scale of the abscissa. Fig.6 shows that decrease in the electrolyte concentration leads to an increase in the selectivity of the membrane, due to its surface charge. The same situation is observed for the symmetrical binary electrolyte KCl (curve *5*), but since the charges of the ions have the same value, the sign of the surface charge in this case does not influence the selectivity.

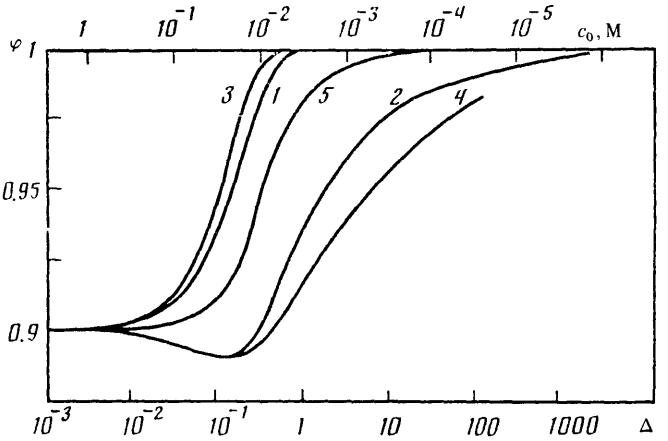


Figure 6. Dependence of the selectivity of a reverse-osmosis membrane on the dimensionless surface charge Δ and on the concentration c_0 of the solutions being separated: *1,2*) $BaCl_2$, *3,4*) $LaCl_3$, *5*) KCl.

The macrokinetic theory examined above for binary solutions[81] has been generalised[82–84] for the case of multicomponent electrolyte solutions. In contrast to the case of binary solutions, in this case the separation involves a change in not only the concentration but also the composition of the solutions. In contrast to the case of binary solutions, in this case the separation involves a change in not only the concentration but also the composition of the solution. The components of the mixture have a mutual influence on one another, whose mechanism is determined by the dependence of the membrane potential $\Delta\psi$ on the composition of the electrolyte solution and the distribution coefficient γ_i for each ion.

This brief review of the present state of the theory of the reverse-osmosis separation of electrolyte solutions shows the great variety of physicochemical factors responsible for the selective action of membranes. Corresponding methods for calculating the selectivity can be developed for each of the retention mechanisms. In real membranes, however, the surface charge, the dielectric exclusion of ions, and the change in the properties of water in the fine pores may exert their influence simultaneously. It is difficult to determine *a priori* the extent of their influence, particularly since there are insufficient data on the structure of the pore space in membranes and on the localisation of the charges and active centres on the surface of the pores and in the bulk of the membrane, which influence both the properties of water and the distribution of ions in

the pore solution. Information on the contribution of a particular mechanism of selectivity can now be obtained by carrying out comprehensive studies of membranes using the procedure developed.[80]

The main qualitative conclusions from the above examination are that for the separation of electrolyte solutions with a low concentration it is necessary to use membranes with a high surface charge, and for the separation of solutions with a higher concentration it is necessary to use membranes whose pore surface is highly hydrophilic. By giving membranes these new properties, it is possible, while retaining fairly high selectivity values, to increase slightly the pore dimensions, and this makes it possible to increase the efficiency or to decrease the expenditure of energy used to pump the solution through the membrane, by using smaller pressure differences.

This also leads to the conclusion that for the separation of solutions with different compositions and concentrations it is necessary to prepare membranes of different types, differing not only in the pore dimensions, as is the case at present, but also in their surface electrical properties and hydrophilic properties.

The main task, whose solution requires the use of the methods of the statistical mechanics of molecular systems and numerical and physicochemical experimental methods, is the refinement of the calculation of the changes in the intrinsic energy of ions in fine pores and the characteristics of the structural state of water. This will make it possible to refine and predict quantitatively the values of the equilibrium distribution coefficients which at present appear as a parameter in the equations of the theory of reverse osmosis.

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Concentration Polarisation in the Electrodialysis Process and the Polarisation Characteristics of Ion-selective Membranes

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Complications in the electrodialysis process, due to the occurrence of concentration polarisation, are analysed. It is shown that most present-day methods for measuring the electrochemical characteristics of ion-selective membranes are not suitable for monitoring the behaviour of these membranes over a wide range of polarising current densities. An analysis of the polarisation characteristics of electromembrane systems shows the advantages of a system with a rotating membrane disc. It is shown that in the polarisation process there is a significant deterioration of the electrochemical properties of heterogeneous membranes whereas the properties of homogeneous perfluorinated sulpho-cation-exchange membranes remain almost unchanged.
The bibliography includes 43 references.

CONTENTS

I. Introduction 585
II. Basic principles of the electrodialysis process 585
III. Polarisation characteristics of ion-selective membranes 587

I. INTRODUCTION

The intensive growth of industry and power engineering, the utilisation of natural resources and the development of agriculture in new areas with limited supplies of fresh water, and the growth of population are creating a shortage of fresh water all over the world. At the same time the increasing volume of sewage is having a deleterious effect on the environment and the condition of the water basins. One of the key questions in the solution of problems of environmental conservation is the development of efficient methods for separating mixtures into their components.

Membrane methods of purifying and concentrating solutions are favoured because of their low energy consumption and material content, simplicity of maintenance, and economy. Of the various membrane technologies electrodialysis has a special place in that it provides unique possibilities for carrying out deionisation and concentration of electrolyte solutions and also synthesis and chemical reactions of various substances. A very widespread application of electrodialysis, both in the USSR and abroad, is the desalination of water. Questions of the theory and practice of electrodialysis are discussed most fully in Wilson's monograph,[1] which retains its value to the present day, and also elsewhere.[2-5] Electrodialysis (ED) is the process of directional transport of ions through an electromembrane system (EMS), which consists of one or several membranes, particularly ion-selective membranes, placed in the electrolyte solution. The driving force of the ED process is the electric potential gradient. In Fig.1 is shown a typical ED scheme employing ion-selective membranes which is used to deionise and concentrate electrolyte solutions. If (as in Fig.1) a stack of alternating cation-selective and anion-selective membranes is placed between a pair of electrodes, then the ions will migrate in equivalent quantities from the solution in the deionisation chambers (*I*), which have anion-selective membranes on the anode side and cation-selective membranes on the cathode side, to the adjacent concentrating chambers (*II*), which have cation-selective membranes on the anode side and anion-selective membranes on the cathode side, and will be removed from the concentrating chambers with the enriched solution (the concentrate).

The rate of transport of the ions through the EMS is determined by the current density and is directly dependent on it. However, the current density is restricted to a limiting value corresponding to the reduction of the ion concentration at the surface of the membrane on the desalination chamber side to zero. The limiting current density depends on the physicochemical properties of the solution undergoing treatment and the membranes and also on the hydrodynamic conditions in the chambers of the electrodialysis equipment, which are dependent on the constructional performance of the chambers and the rate of flow of the solution.

The concentration polarisation of the EMS which occurs as a result of the diffusion constraints leads to high energy consumption and also favours the deposition of precipitates of sparingly soluble salts and hydroxides on the membrane surfaces, so reducing the efficiency of the ED process.

II. BASIC PRINCIPLES OF THE ELECTRODIALYSIS PROCESS

The requirements imposed on electrodialysis apparatuses and on the organisation of the electrolyte deionisation process in them are determined by the interrelation between technological parameters that are governed by the state of the EMS.

The concentrations of the solutions remain constant in the central part of the flow and vary only within the so-called diffusion layers, which are adjacent to the surfaces of the ion-selective membranes. The thickness of a diffusion layer is an arbitrary concept and is defined by the coordinate (on an axis perpendicular to the membrane surface) at which the concentration of the solution differs from the concentration in the central part of the flow by 1%. The variation in the concentration in the diffusion layer is caused by the difference in the transport numbers of the ions in the solution and membrane phases. When the density of the current passing through the electromembrane system is increased the concentration of the diluate at the surface of the membrane falls. The limiting current density is the density at which this concentration approaches zero.

The state of the EMS can be regarded as defined if we know how the electric potential is distributed in it and also the concentrations and rates of flow of the working solutions. A theoretical analysis of the mass exchange in the ED process reduces to the solution of

equations for electrodiffusion and convective diffusion. These equations, together with the equation of motion, the conditions of continuity and electroneutrality of the solution, and also the equation for the current density at the solution–membrane interfaces, form a closed system of equations.

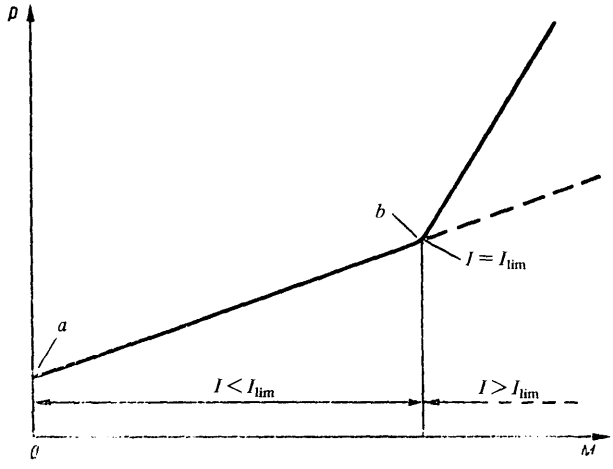


Figure 2. Relationship between the energy consumption P (calculated per unit mass) and the specific mass-transport M in the electrodialysis process.[4]

The relationship between the energy consumed in the electrodialysis and the amount of material transported across the effective area of the membrane in unit time is shown in Fig.2. Point *a* corresponds to the minimum energy consumption (P_{min}) required to achieve a given degree of deionisation in the absence of concentration polarisation and ohmic resistance of the solution and the membranes, and with a number of ther assumptions:[1]

$$P_{min} = 2RT\left(\frac{\ln(c_i/c_0)}{1-c_i/c_0} - \frac{\ln(c_i/c_c)}{1-c_i/c_c}\right)$$

where P_{min} is the minimum specific (i.e. per unit mass transferred) energy consumption, c_i and c_0 are the initial and final concentrations of the diluate, and c_c is the concentration of the mother liquor.

Point *b* corresponds to the limiting current density; on the section *ab* there is a proportionate increase in the specific energy consumption as the mass transport through the EMS increases. However, at current densities above the limiting value (the section to the right of point *b*) the slope of the curve changes, indicating unproductive energy consumption. To achieve a given degree of deionisation of the solution being treated it is possible, having increased the specific mass transport, to reduce the effective area of the ion-selective membranes correspondingly, e.g. by reducing the number of working chambers in the electrodialysis apparatus.

To intensify the ED process the working current density in the electrodialysis apparatus should be increased to its limiting value. To increase the limiting current density, i.e. to remove the diffusion constraints, the construction of the electrodialysis apparatus must be further perfected and the electrochemical properties of the ion-selective membranes improved.

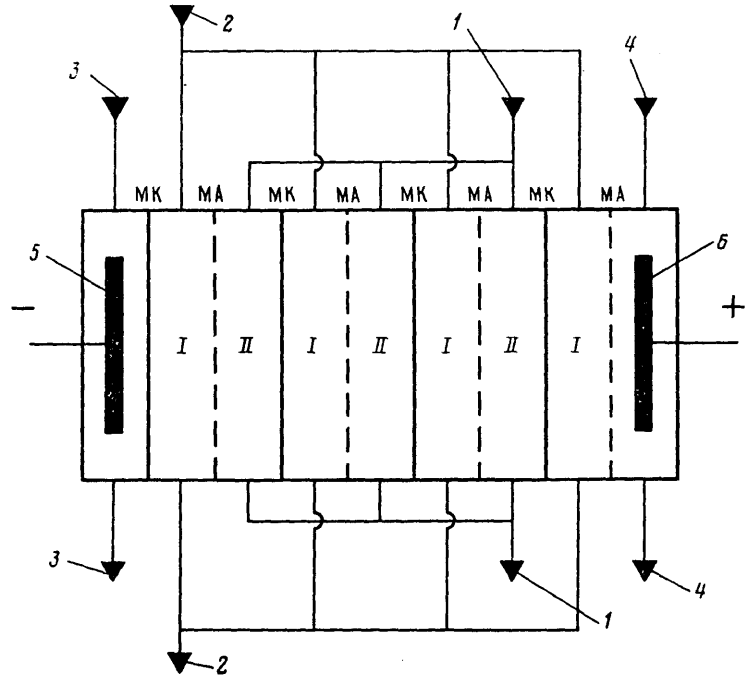


Figure 1. Diagram of an electrodialysis process using ion-selective membranes: MK) cation-selective membrane; MA) anion-selective membrane; *1*) deionisation channel; *2*) concentrating channel; *3*, *4*) channels for flushing electrode chambers; *5*) cathode; *6*) anode.[4]

III. POLARISATION CHARACTERISTICS OF ION-SELECTIVE MEMBRANES

In spite of the progress achieved in investigating the mechanism of electro-mass-transport in an EMS (which is substantially different at current densities below and above the limiting diffusion value[6-11]), most current methods of measuring the electrochemical properties of membranes (see, for example, a previous review[12]) do not make it possible to assess the behaviour of the membrane under investigation over a wide range of variation of the polarising current. This relates primarily to the monitoring of the selectivity of membranes through the transport numbers of the ions,[1,3,12] which remain constant only for small variations in the concentrations of the ions in the membrane phase.[13] The most promising methods for estimating the electrical conductivity of membranes are, in our opinion, those which enable the resistance of the EMS to be measured during the process of their polarisation.[14,15]

A study of the volt-ampere curves of the EMS enables the mechanism of electro-mass-transport in these systems under different polarisation conditions to be judged.[16-23] In most of this work the EMS's are investigated with a flowing solution although, owing to the difference in accessibility of the membrane surfaces as regards diffusion, a detailed study of the ion-transport mechanism in this type of system is difficult in principle. In other work[24-28] EMS's with free convection are examined because in the systems, in contrast to the flow type, identical thicknesses of the diffusion layers can be obtained.

In classical electrochemistry there is a system with forced convection, which is unique in its way and which ensures equal accessibility of the electrode surface as regards diffusion; this is the rotating disc electrode (RDE).[29,30] The theory of such a system has also been developed.[31] The first attempts to apply the RDE method to electro-membrane systems were reported in Ref.32 and later in Ref.33. They have, however, remained virtually undeveloped owing to the technical complexity of the experiment. The main defect in the apparatus that was proposed[32] is caused by mounting the membrane under investigation on a spindle with the aid of a nut; this disturbs the equal accessibility of the surface and the hydrodynamics of the system. A common defect of the apparatuses developed in Refs.32 and 33 is that the desalination and concentrating chambers adjacent to the membrane are not equivalent and this fundamentally limits the range of possible investigations.

An apparatus with a vertically aligned rotating membrane, which separates symmetrical immovable half-cells with polarising and measuring electrodes filled with solution, has been described.[34] We presume that precisely this type of EMS is suitable for use in studying the polarisation characteristics of membranes because, under conditions of equal accessibility of the membrane surfaces in respect of diffusion and with the possibility of accurate calculation of the thickness of the diffusion layer, the polarisation characteristics of the system can be analysed and the extra-diffusion stage of the electro-mass-transport isolated.

A disadvantage of voltammetry with linear scanning of the flow, as applied to an EMS, especially when dilute solutions are used, is the large drop in voltage in the regions between the membrane and the measuring electrodes, as a result of which there is a reduction in the accuracy of recording the overvoltages associated with the limiting stages of the electro-mass-transport. To eliminate the ohmic drop in voltage in the solution, which is not connected with the concentration polarisation processes, compensating measuring circuits are devised. A circuit similar to that proposed in Refs.35 and 36 is shown in Fig.3. The membrane being examined (*1*) is in a cell which contains, in addition to the polarising (*2*, *3*) and measuring (*4*, *5*) electrodes, a further electrode (*6*). First, in the absence of concentration polarisation on input of an alternating current pulse to the polarising electrodes, the amplification factor of the second differential amplifier DU2 is chosen so that the difference in the voltage drops between the probes *4* and *5* on the one hand, and *5* and *6* on the other, which is registered by the recording graph plotter, is equal to zero. Then, on input of a linearly increasing current from the

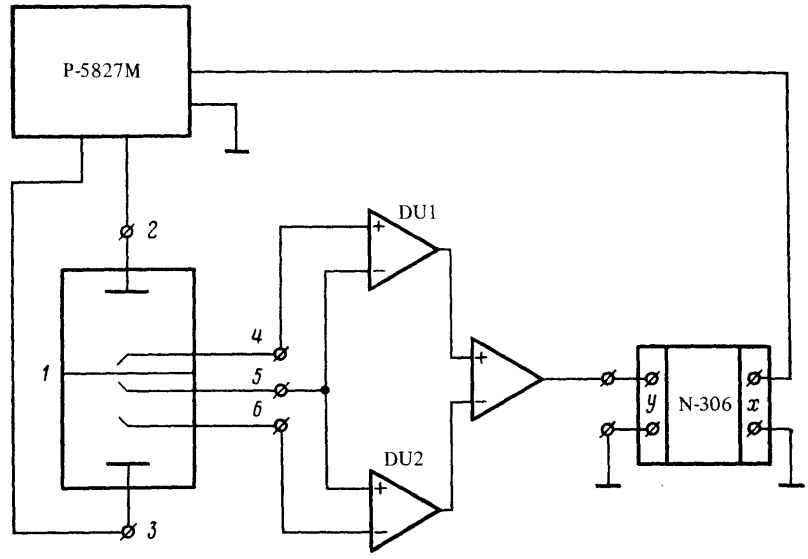


Figure 3. Block diagram of the apparatus for obtaining the volt-ampere characteristics of an EMS: P-5827M) potentiostat; N-306) graph plotter; DU1, DU2) differential amplifiers.

potentiostat, the volt-ampere curves registered by the recorder reflect the change in the voltage drop in the EMS due to concentration polarisation.

Specimens of well known commercial brands of membrane have been examined. The heterogeneous membranes MK-40, MA-40, and MA-41,[37] used in electrodialysis processes, are hydrophilic and possess a "porous" structure containing unexchangeable absorbed solution. The homogeneous perfluorinated sulpho-cation-exchange membranes (PSM), which have their main use in chlorine electrolysis processes,[38] are hydrophobic and in dilute solutions have properties close to the ideal selective membrane.

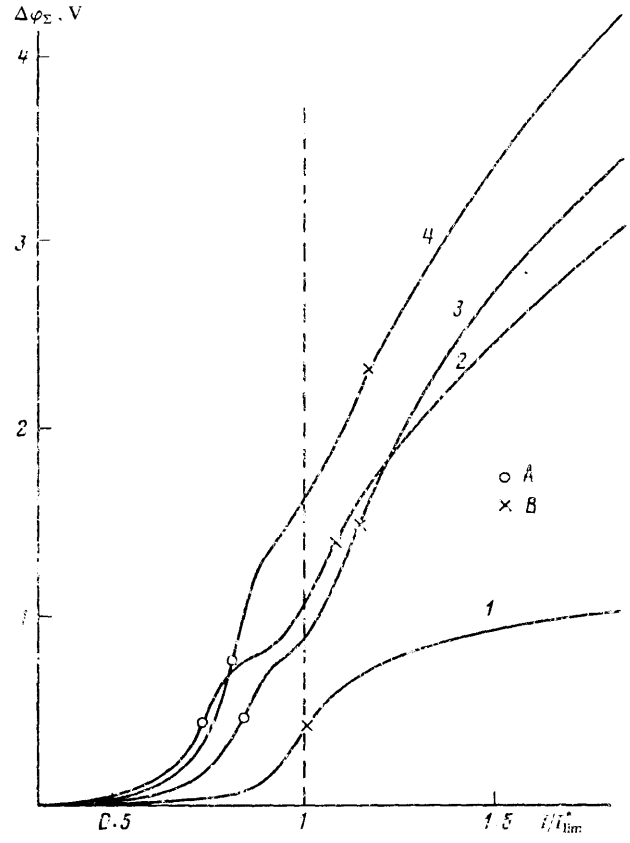


Figure 4. Volt-ampere curves for EMS's with the membranes: *1*) PSM; *2*) MA-41; *3*) MK-40; *4*) MA-40.

The volt-ampere curves shown in Fig.4 were obtained for the commercial grade membranes in 0.01 M sodium chloride solution with the membrane disc rotated at 100 rev min^{-1}, corresponding to a diffusion layer thickness $\delta = 5.8 \times 10^{-3}$ cm.[31] The possibility that the theory developed in Ref.16 is applicable to the system being used is confirmed by the occurrence of a characteristic linear dependence of the limiting current density on the square root of the angular velocity of rotation of the disc; this dependence is satisfied in the range of speeds 100–600 rev min^{-1}. In Fig.4 the dimensionless current density quantity I/I^*_{lim} (where I^*_{lim} is the limiting electrodiffusion current density for an ideally selective membrane) is plotted along the abscissa axis. In a solution of a binary electrolyte the following relationships are satisfied:[29,39]

$$I^*_{lim} = \frac{z_1 F D^* c_0}{(1 - t_1)\,\delta} \tag{1}$$

and

$$\delta = 1.61\,(D^*)^{1/3} \nu^{1/6} \omega^{-1/2}$$

where c_0 is the initial concentration of the solution, δ is the thickness of the diffusion layer, F the faraday, D^* the diffusion coefficient of the electrolyte solution, z_1 the charge number of the counter ion, ν the kinematic viscosity, and ω the angular velocity of rotation of the disc.

The volt-ampere curve for a homogeneous PSM is characterised by a relatively small voltage drop in the polarisation process: at the inflection point corresponding to the limiting current density I_{lim} the drop is 440 ± 30 mV. This is close to the value (450 mV) calculated using an equation obtained from Ref.40 and subtracting the ohmic voltage drop in the solution, which is not connected with concentration polarisation processes:

$$\Delta\varphi_\Sigma = 2\Delta\varphi_M + \frac{RT}{z_1 F} \ln\left\{\frac{[1 + \exp(\Delta\psi_M)]^2}{4\exp(\Delta\psi_M)}\right\}$$
$$\Delta\psi_M = \Delta\varphi_M \frac{z_1 F}{RT} \tag{2}$$

The membrane potential $\Delta\phi_M$ is determined by the diffusion relaxation method developed in Refs.26 and 28. The value $\Delta\phi_\Sigma$ can be used to estimate the polarisability of the membrane and the quantity $I_{lim} \cdot \Delta\phi_\Sigma$ characterises the energy consumption on polarisation of the system in the limiting state.

If the surface of the homogeneous PSM on the desalination chamber side is rubbed with emery paper the limiting current density decreases and the voltage drop increases, indicating a partial extension of the diffusion constraints on the transport of ions into the membrane phase because of the increased roughness of its surface.

The inflection point on the volt-ampere curve for the PSM (Fig.4) is displaced slightly to the right with respect to the limiting current density for an ideally selective membrane, I^*_{lim}. This indicates that the selectivity of the membrane is non-ideal. To estimate the reduction in selectivity we introduce a dimensionless quantity representing the displacement of the limiting current density for this membrane relative to the ideally selective membrane:

$$s = \frac{I_{lim} - I^*_{lim}}{I^*_{lim}} \tag{3}$$

The relative displacement for the PSM is 0.02, showing that it has a high selectivity.

On the volt-ampere curves for the heterogeneous membranes (Fig.4) two inflection points, to the left and right of I^*_{lim}, can be found using the three tangent method. If the displacement of the first point (point *A* in Fig.4) is evaluated using expression (3) it will be negative and that of the second point (point *B* in Fig.4) will be positive. The heterogeneous membranes investigated contained from 11 to 20 vol.% of equilibrium solution.[41] It is therefore likely that concentration polarisation in EMS's containing heterogeneous membranes involves both a near-membrane region in the solution, defined by the size of the δ-layer, and a near-surface region in the membrane pores occupied by the unexchangeably absorbed electrolyte, which can be defined by an effective thickness $\bar{\delta}$. The current density values corresponding to the *A* points in Fig.4 are probably

the limiting current densities in the $(\delta + \bar{\delta})$-layers whereas the *B* points represent the onset of the limiting state in the δ-layers of the "free" solution.

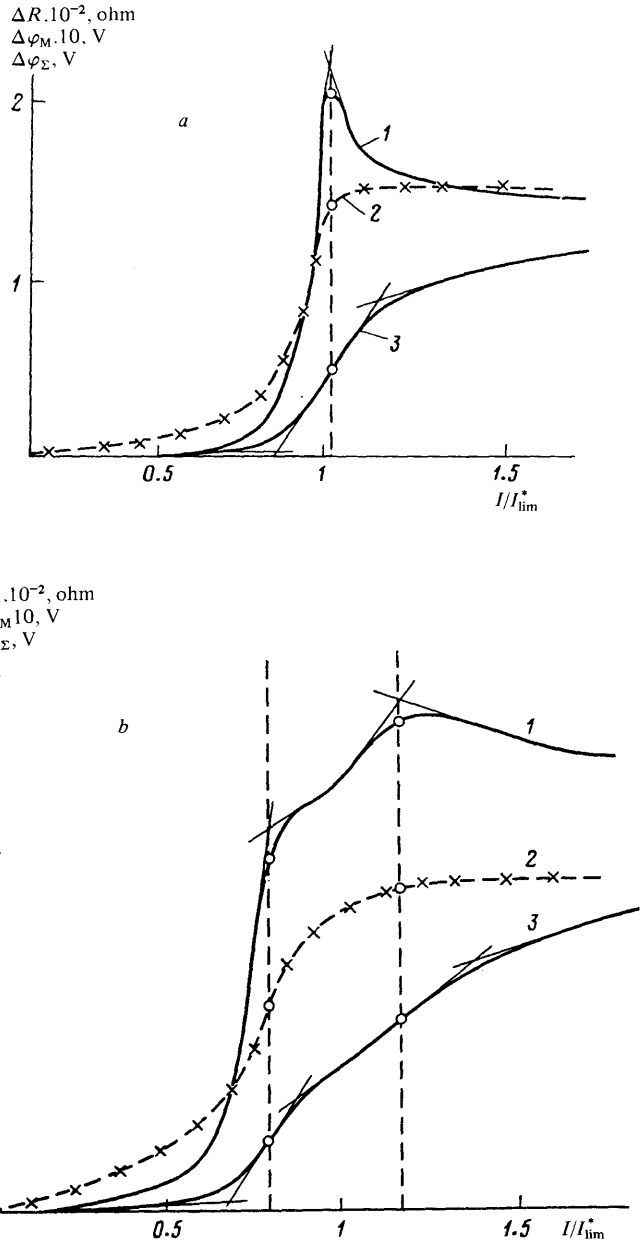


Figure 5. Plots of the change in resistance (*1*), membrane potential (*2*), and total voltage drop (*3*) against the dimensionless current density for EMS's with the membranes: *a*) PSM; *b*) MK-40. 0.01 M NaCl solution, rate of rotation of the membrane disc = 100 rev min^{-1}.

Thus the first inflection point on the volt-ampere curve is probably associated with the concentration polarisation which is due to the diffusion constraints on the transport of ions in the solution contained in the heterogeneous membrane phase. The value of the current density $\bar{I}_{lim}$ corresponding to this sudden change in the difference between the potentials can be termed the limiting current density for the equilibrium solution of the membrane. This is confirmed by the weak dependence of $\bar{I}_{lim}$ on the rate of rotation of the membrane.

To test the stated assumptions and to locate the inflection points on the volt-ampere curves more accurately by using the method described in detail in Refs.42 and 43, the ohmic resistance of the EMS in the polarisation process was determined. In Fig.5 the volt-ampere curves are compared with the variation of the resistance with current density for EMS's with PSM (Fig.5*a*) and MK-40 (Fig.5*b*) membranes, identical conditions being used. In the first case the inflection point on the volt-ampere curve coincides with the maximum on the curve for ΔR as a function of I/I^*_{lim} and corresponds to the limiting electrodiffusion current density in the solution. For the MK-40 membrane the $\Delta R(I)$ curve shows two local maxima which coincide with the inflection points on the volt-ampere curve corresponding to the negative and positive relative displacement of the limiting current density.

Fig.5 also shows the dependence of the membrane potential $\Delta\phi_M$ on the dimensionless current density, as obtained by the diffusion relaxation method.[28] For the homogeneous PSM $\Delta\phi_M$ reaches a maximum at I_{lim} and then shows hardly any change. For the MK-40 membrane the sharp jump in $\Delta\phi_M$ begins at the limiting current density in the equilibrium solution of the membrane $\bar{I}_{lim}$ but the membrane potential reaches saturation only at a current density equal to the limiting electrodiffusion current density in the free solution I_{lim}, which is determined from the second inflection point on the volt-ampere curve.

This is confirmed by an analysis of curves, obtained under similar conditions,[28,29] showing the decrease in the membrane potential with time for PSM and MK-40 membranes at different current densities (Fig.6). Fig.6 also shows curves calculated assuming purely extra-diffusion kinetics for the process. For the PSM the observed and calculated curves agree. The reason for the slightly larger experimental values of $\Delta\phi_M$ is probably that the value of the liquid diffusion potential was not taken into account in the calculation. In the case of the MK-40 membrane the drop in the membrane potential in the first 0.1 s is considerably more rapid than would be expected if purely extra-diffusion processes took place; the experimental curves lie considerably above the calculated curves. Similar results were obtained for the heterogeneous membranes MA-40, MA-41I, and also MK-44 and MK-41, indicating that they are strongly polarisable compared to homogeneous membranes.

Analysis of results obtained by independent methods suggests that concentration polarisation of an EMS is due to both intra- and extra-diffusion constraints on electro-mass-transport. With the heterogeneous membranes MK-40, MK-44, MK-41, MA-40, and MA-41 the diffusion constraints on the transport of ions in the membrane phase permit a limiting state to be reached at current densities I_{lim} smaller than the limiting current density for an ideally selective membrane I^*_{lim}. A further increase in the current leads to the establishment of a limiting state in the free solution at current densities $I_{lim} > I^*_{lim}$, indicating non-ideal selectivity of the heterogeneous membranes. The relative displacement of the limiting current density *s* gives a quantitative description of the selectivity of the membranes in the limiting state and the product $I_{lim}.\Delta\phi_\Sigma$ gives the energy consumption on polarisation of the membrane.

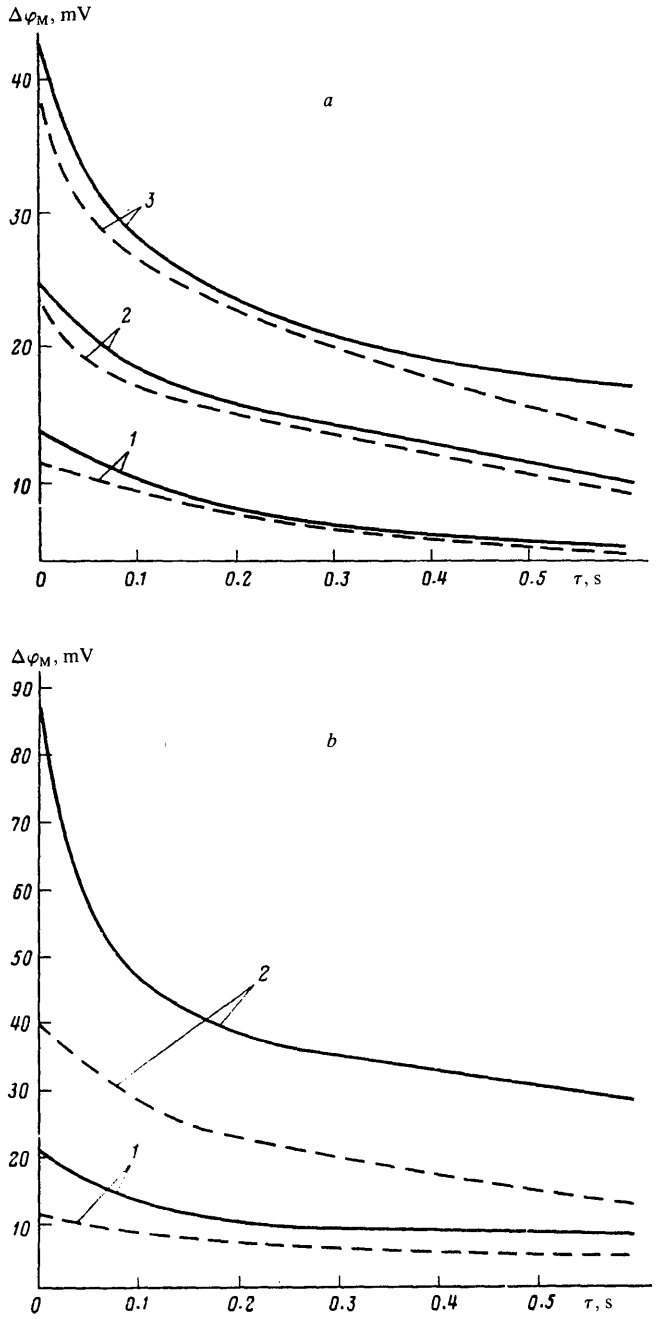


Figure 6. Experimental (full lines) and calculated (broken lines) curves showing the decrease in the membrane potential for a PSM (*a*) and an MK-40 membrane (*b*) with time after switching-off the polarising current. Polarising current density (mA cm^{-2}): *1*) 1; *2*) 2; *3*) 3; rate of rotatation of the membrane disc 100 rev min^{-1}, 0.01 M NaCl solution.

The values of the limiting electrodiffusion current densities, their displacements, and the voltage drops corresponding to $\bar{I}_{lim}$ and I_{lim} (see Table) can be used to judge the energy consumption on polarisation of the membranes and their selectivity; in our opinion this provides fairly full information on the electrochemical behaviour of membranes in the polarisation process.

Polarisation characteristics of EMS's containing different membranes.*

Membrane	10^3c, M	I^*_{lim}, mA cm^{-2}	$\bar{I}_{lim}$, mA cm^{-2}	$\bar{s}$	$\Delta\bar{\varphi}_\Sigma$, mV	I_{lim}, mA cm^{-2}	s	$\Delta\varphi_\Sigma$, mV
PSM	11.5	5.0	—	—	440	5.1	+0.02	440
MK-40	10.0	4.2	3.5	−0.17	450	5.1	+0.21	1750
MA-41I	10.0	6.75	4.6	−0.32	280	8.2	+0.21	1680
MA-40	10.0	6.75	5.2	−0.23	680	7.6	+0.13	2200

* The parameters $\bar{I}_{lim}$, $\bar{s}$, and $\Delta\bar{\phi}_\Sigma$ describe the membrane phase.

The data in the Table indicate that the heterogeneous membranes MK-40, MA-40, and MA-41 have a negative value of s as well as a positive value and this is explained by their polarisability owing to the presence of unexchangeably absorbed electrolyte in the membrane phase. The homogeneous PSM has only a positive displacement which is much smaller than the corresponding values for the heterogeneous membranes; this indicates that it has a high selectivity whereas the selectivities of the heterogeneous membranes in the polarisation process are reduced. The values of $\Delta\phi_\Sigma$ for the heterogeneous membranes, which are much larger (by a factor of 4—5) than the corresponding value for the PSM, typify a higher energy capacity of processes with heterogeneous membranes.

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Analysis of the polarisation characteristics of an EMS in a system with a rotating membrane disc thus indicates that the limiting stage of the mass transport through heterogeneous membranes is internal diffusion when the current density is below the limiting value for an ideally selective membrane but external diffusion at current densities above I^*_{lim}. Polarisation of the membrane entails a reduction in its selectivity and an increase in the electrical resistance of the system. When homogeneous PSM's are polarised the mass-transport process takes place under extra-diffusion control.

In other words, in the polarisation process heterogeneous membranes which contain a sufficient amount of the equilibrium solution display a considerable deterioration in their electrochemical properties. In this case increasing the intensity of the electrodialysis process only by removing the extra-diffusion constraints will be not be sufficiently effective. Consequently, in our opinion, special attention must be given to the production of new, desirably homogeneous types of membrane.

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Bacteriorhodopsin as a Possible Element of Membrane Bioreactors

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Certain approaches to the creation of membrane bioreactors, representing an example of integrated membrane systems, are examined. The characteristic features of the use of organised molecular assemblies in such systems as sensor and regulatory elements are discussed. The properties of the retinal-protein complex of bacteriorhodopsin as a promising component of integrated membrane systems, capable of carrying out regulatory functions, are examined.
The bibliography includes 139 references.

CONTENTS

I. Introduction 592
II. Membrane bioreactors 592
III. Functional properties of bacteriorhodopsin in artificial systems 597

I. INTRODUCTION

The application of membrane technology in modern industry makes it possible to economise on resources and energy and to reduce greatly the influence of unfavourable factors on the environment. In recent years a tendency has arisen in membrane research to combine various processes, since "integration" of technological stages makes it possible to make the best use of the potential advantages of membrane systems. This procedure represents the embodying of the principles constituting the basis of the functioning of biological systems, which are distinguished by the specificity and interdependence of processes, the combination of a number of functions in a single element, and the existence of regulatory mechanisms at various stages of the process.[1] An excellent example of integrated photochemical processes is natural photosynthesis. It includes the collection of solar energy by the chlorophyll of the antenna and by other pigments, the transfer of the excitation energy to the reaction centre, the separation of charges in the photosystems I and II, electron transfer, and other processes.[2] The concept of "integrated membrane systems" presupposes not only the application of various membranes in successive separation stages, but also the combination of functions, for example, the coupling of chemical reactions with membrane separation, the incorporation in the system of membrane sensors for the control of the dynamics and optimisation of the processes, etc.[3] It may be expected that the combined application of membrane systems will prove most effective in fields such as agroindustry, petrochemistry, biotechnology, and the processing of sewage.

II. MEMBRANE BIOREACTORS

1. Membranes in Chemical Reactions

One of the vigorously developing branches of membrane technology involves the creation of membrane reactors (MR) in which the reaction products (or one of the products) are separated from the reaction mixture. The advantages of MR are manifested particularly in carrying out reversible reactions: the continuous removal of the products shifts the reaction in the forward direction and makes it possible to achieve a high degree of conversion of the starting materials. One of the possible ways of carrying out such a process is associated with the use of selective gas separation membranes.[4,5] A schematic illustration of a MR of this type is presented in Fig.1. (Since questions concerning membrane catalysis are considered in detail in another review in the present issue of the journal,[1] we shall confine ourselves to only certain examples). The non-equilibrium nature of the process in this type of flow MR with a microporous glass membrane made it possible to increase the degree of conversion of cyclohexane into benzene by a factor of ~2.5 compared with the equilibrium value. The advantages of the MR are manifested particularly clearly when a palladium membrane, permeable exclusively to H_2, is used.[4] In this case the degree of conversion of cyclohexane reaches 99.5% and, when the flow rates of the starting material and inert carrier gas are suitably selected, it can be increased still further. Thus benzene becomes virtually the only component at the outlet from the MR, which eliminates the necessity for the separation of benzene and cyclohexane, reducing considerably thereby the cost of the industrial manufacturing process.

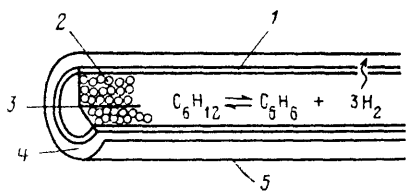


Figure 1. Schematic illustration of a membrane reactor with a palladium membrane for the dehydrogenation of cyclohexane:[4] 1) palladium membrane; 2) catalyst; 3) cyclohexane; 4) inert carrier gas; 5) shell.

Another most imporatant trend in the development of the MR is the study of the properties of catalysts stabilised on polymer membranes. In this case the membrane plays the role of a medium in which a high local concentration of the reactants and the necessary

environment can be created. A large number of studies have been devoted to the photocatalytic decomposition of hydrogen sulphide in the presence of colloidal CdS immobilised on a fluorine-containing cation-exchange membrane of the Nafion type.[6-8] The internal structure of membranes of this type simulates the structure of the inverted micelles, because it includes ionic structures connected by channels and incorporated in the hydrophobic fluorocarbon phase.[9,10] Cationic substrates sorbed in the membrane channels from the aqueous phase are acted upon by a powerful electric field,[11] which apparently must be taken into account in considering the catalytic properties of the complexes. The high chemical stability of the perfluorinated polymer membranes makes it possible to employ them in corrosive media over a wide temperature range. The photodecomposition of H_2S has aroused interest in connection with the search for non-traditional energy carriers, to which the molecular hydrogen obtained as a result of the reaction belongs. Furthermore, it is possible to reduce in this way the effect of the environment by toxic sulphur compounds, many tonnes of which are evolved as waste in chemical, metallurgical, and petrochemical industries.[6] Finally, elemental sulphur, the secondary reaction product, is a valuable raw material and natural gas deposits with a high hydrogen sulphide content may serve as its source.

Another possible application of membrane photocatalysts for the solution of ecological problems is associated with the purification of sewage. The photodegradation of chlorophenols in aqueous solutions, activated by doping with polyphenylacetylene immobilised on a poly(vinyl chloride) membrane, has been investigated.[12] The immobilisation of polyphenylacetylene makes it possible to stabilise it, preventing, in particular, the liberation of the doping agent. The rate of photodecomposition of organic impurities increases significantly with increase in the electrical conductivity of the membrane. It has been suggested that the mechanism of the photodegradation includes the formation of intermediate radical states, while the presence in the membrane of an organic conductor with electronic conductivity permits photoinitiation and accelerates oxidation-reduction processes.

2. Membrane Bioreactors

The development of MR in which chemical reactions take place under the influence of catalysts of biological origin has expanded greatly in recent years. Apparatus of this kind is referred to as membrane bioreactors (MBR). The solution of a set of problems associated with the application of MBR, including the manufacture, isolation, and purification of enzymes and their use as immobilised biocatalysts, is nowadays a leading branch of biotechnology. Membranes serve as a cheap and reliable base for the immobilisation of enzymes and for the creation of compact and flexible devices in which the separation process is coupled with a chemical reaction. Biocatalysts are placed on one side of a suitable membrane, the substrate is brought into contact with the biocatalyst, and the resulting product, whose molecules must be fairly small, permeates through the membrane. This general principle of the design of MBR has been applied in the following main types of MBR used, differing in configuration and the reaction conditions:[13] (1) membrane modules combined with a reaction compartment which contains the biocatalyst in a dissolved form; (2) reactors with membranes in the form of hollow fibres in which the enzyme is usually located on the outer side of the membrane, while the substrate circulates through the inner space within the fibres; (3) reactors with a membrane made of a mouldable solution containing the biocatalyst; (4) reactors with the enzyme fixed by cross-links on a microporous film or grafted covalently to the latter.

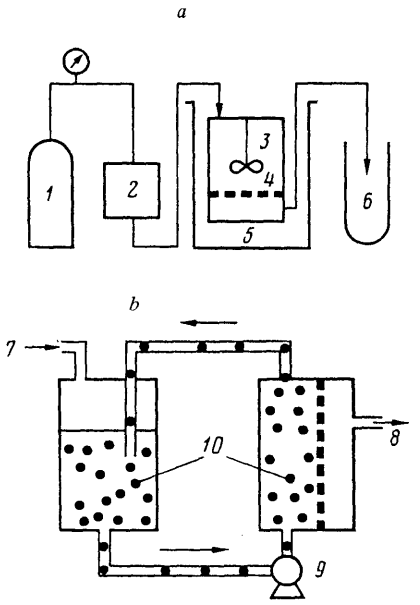


Figure 2. Membrane bioreactors with continuous mixing:[18] *a*) direct filtration reactor: 1) gas cylinder for the establishment of the transmembrane pressure; 2) compartment with the substrate; 3) reaction vessel with stirrer; 4) membrane; 5) thermostatted compartment; 6) vessel for the product; *b*) membrane flow bioreactor: 7) initial mixture; 8) product; 9) pump; 10) biocatalyst.

The appearance of MBR of the first type became possible after the creation in 1965 of the ultrafiltration membrane,[14] which was used to concentrate enzymes.[15,16] In 1970 the first membrane bioreactor was constructed in which a solution of α-amylase from *B.subtilis* was used to hydrolyse starch.[17] A considerable proportion of the enzymes used as biocatalysts have molecular weights ranging from 10 to 100 kDa and are retained by membranes designed for ultrafiltration. Reactors of the first type operate under ideal mixing conditions and are most suitable for reactions inhibited by the product, since the latter is continuously removed as it is formed, which increases the yield. Two varieties of ideal mixing MBR, differing in the organisation of the substrate and product streams are known (Fig.2).[18] Fig.2*a* presents a scheme for a MBR operating under direct filtration conditions. A significant disadvantage of such MBR is the contamination of the membrane and also concentration polarisation, the elimination of which requires vigorous stirring of the contents of the reaction compartment. Reactors constructed in accordance with the above scheme are used mainly for laboratory research. A flow MBR free from the above disadvantages was first proposed by Porter and Michaels[19] (Fig.2*b*). In contrast to the scheme in Fig.2, the separating membrane module is in this case physically separated from the reaction vessel containing enzymes or whole cells as the catalyst. The flow MBR makes it possible to use

the biocatalyst repeatedly and to organise the operation of the system under stationary conditions. Reactors of this type are suitable for industrial use, for example, in apparatus for the treatment of sewage.[20,21] For the normal functioning of MBR of the type considered, it is essential that the product molecules should be significantly smaller than the substrate and biocatalyst molecules. By virtue of this limitation, MBR of the given type have found applications mainly in the hydrolysis of proteins, starch, and cellulose.[18] Low concentrations of the components and relatively low rates of conversion are characteristic of the MBR operating under ideal mixing conditions.

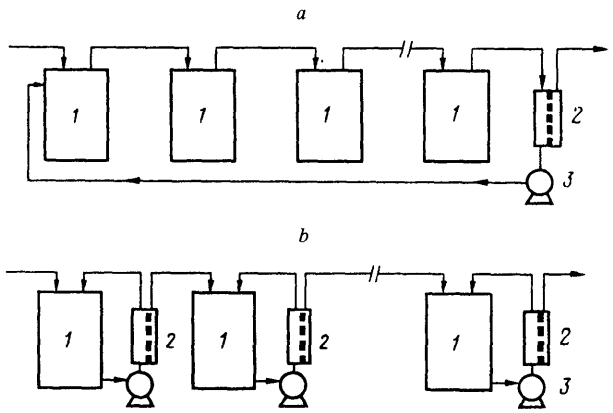


Figure 3. Cascade membrane bioreactors with modules for membrane separation in the concluding stage (*a*) and in each stage (*b*): 1) reactor; 2) membrane separation unit; 3) pump.[18]

The search for highly productive systems, in which a high degree of conversion of the starting material is attained, led to the creation of cascade MBR (Fig.3).[18] Two types of cascades are used: with the membrane separation unit in the concluding stage (Fig.3*a*) and with recirculation of the unreacted component at each stage (Fig.3*b*). Cascade systems of the later type are fairly expensive but ensure a high flexibility of the system, since they create the possibility of carrying out each stage under optimum conditions, which is especially convenient for multienzyme processes.

A higher degree of integration of the chemical reaction and the membranes separator is achieved in MBR based on hollow fibres, since in such devices the membrane separation cell also functions as the reactor. The principal advantage of devices based on hollow fibres is a high ratio of the membrane's surface area to the volume which it occupies. Furthermore, the operating conditions for such MBR approach the ideal displacement regime, which permits the attainment of a high degree of conversion of the substrate. A MBR based on commercial hollow fibres in which an enzyme is enclosed was first described by Rony.[22] Subsequently different versions of hollow fibre MBR, representing two main configurations (Figs.4*a* and 4*b*), were proposed. In the scheme illustrated in Fig.4*a*, the enzyme is deposited on the outer surface of a hollow fibre and the substrate flows through its interior. The products can be removed either from the outer side or from the inner volume within the fibre. Preliminary ultrafiltration of an enzyme solution or a cell suspension through the membrane is widely used for the deposition of the biocatalyst on the surface of the hollow fibre. For example, yeast cells have been deposited in this way on the outer surfaces of ultrafiltration hollow fibres.[23] The cells are then fixed quite firmly in order to ensure the operation of the MBR in the course of ~12 days. The yield of the reaction product is directly proportional to the amount of cells charged into the reactor, but, for a high charge density, there is a sharp increase in the pressure necessary to maintain an acceptable rate of passage of the substrate. An appreciable increase in the transmembrane pressure is undesirable, since under these conditions the biocatalyst is washed off the fibres at a much higher rate. The method of fixation of enzymes by means of physical adsorption has many advantages: a simple and universal deposition procedure, the reduction to a minimum of the steric hindrance in the microenvironment of the enzyme, which is accompanied by an insignificant loss of its activity, and also the absence of the necessity for the introduction of any additives to the biocatalyst, which facilitates the formation of sterile preparations.

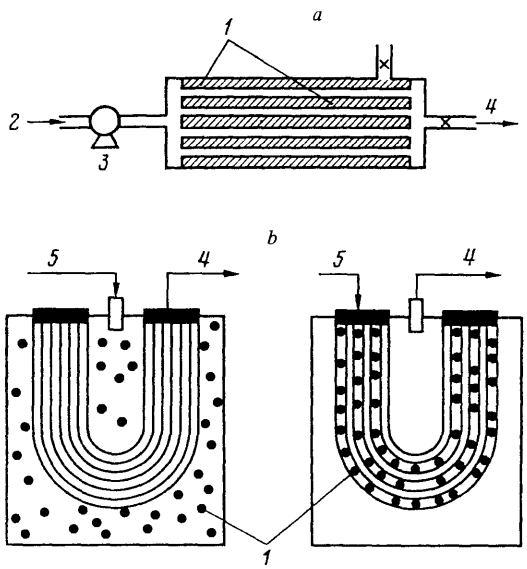


Figure 4. Principal configurations of bioreactors with membranes in the form of hollow fibres: *a*) bunch of fibres in a shell; *b*) bunch of fibres in a compartment containing the biocatalyst or serving for the removal of product; 1) biocatalyst; 2) initial mixture; 3) pump; 4) product; 5) substrate.[18]

The hydrolysis of triglycerides with formation of aliphatic acids and glycerol belongs to the class of technically important reactions. This reaction has been achieved[24,25] in MBR constructed in the form of a module with hollow aromatic polyamide fibres. The hydrolysis of triglycerides from vegetable oils occurred in the presence of lipase from *Candida cylindracea* immobilised on the inner surfaces of the hollow fibres. The enzyme was immobilised by the preliminar ultrafiltration of an aqueous solution of the lipase through the hollow fibres. The substrate—a vegetable oil emulsion—was supplied continuously into the interior of the hollow fibres. The polyamide

membrane is permeable to only one of the reaction products – glycerol, which diffused into the aqueous phase on the outer side of the fibre. Aliphatic acids were removed from the MBR as part of the composition of the lipid phase. The polyamide fibre ensures an effective separation of the phases without their dispersion in any way. Hollow fibre MBR permit the attainment of ~90% conversion of the substrate in 2–3 h,[25] and the time of the stable operation of the system is more than three weeks. A MBR of analogous design has been used for the large scale preparation of 6-aminopenicillanic acid.[26]

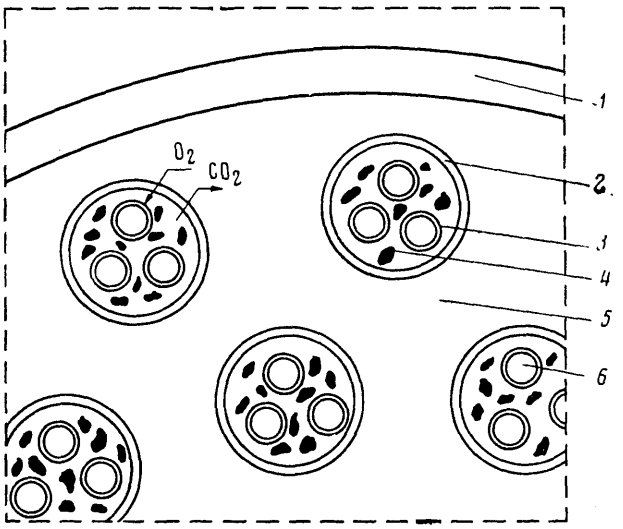


Figure 5. Cross-section through a bioreactor with a double hollow fibre:[28] 1) glass tube; 2) silicone tube; 3) polypropylene hollow fibre; 4) immobilised cells; 5) gas phase; 6) liquid phase.

One of the limitations imposed on the employment of hollow fibre MBR is that the substrate and product must have a low molecular weight, permitting their diffusion through the membrane. This is why such reactors are frequently used for the hydrolysis of oligomers.[18] Another main disadvantage of apparatus based on hollow fibres, already noted in the first relevent investigation,[22] is the limitation of the rate of the chemical reaction by diffusion processes. For example, when MBR with hollow fibres made of polypropylene were used for the production of phenylalanine by mutant strains of *E.coli*,[27] it was observed that the rate of the chemical reaction is limited by the diffusion of oxygen, necessary for the metabolism of the above cells. It has been suggested that reactors of this type are more suitable for systems with a low consumption of oxygen or when anaerobic organisms are employed. Analogous difficulties arise also when gases are evolved in the course of the enzymic reaction. The attempts to overcome these limitations led to the creation of MBR based on double hollow fibres.[28] Fig.5 illustrates schematically the design of a double hollow fibre bioreactor suitable for the cultivation of aerobic cells. The micro-organisms are located in the space between silicone tubes through the walls of which oxygen permeates and hollow polypropylene fibres through which the liquid phase passes. The productivity of the MBR based on double hollow fibres can exceed by a factor of 20–30 that of the traditional enzyme reactors.

MBR are known in which the biocatalyst is enclosed in a porous polymer matrix.[13] The biocatalysts may consist of enzymes or whole cells resistant to the action of the organic solvents used in the formation of the membrane. Many bioreactors of this type have been developed for the processes used in the food industry. In order to combine in a single cell ultrafiltration and the hydrolysis of lcatose in milk and whey, a planar version of the MBR has been proposed.[13] Lactose is immobilised in a microporous poly(vinyl chloride) film placed directly behind the ultrafiltration membrane (Fig.6). The coupling of the processes makes it possible to avoid the undesirable contact between the enzyme and particles of milk fat. An analogous process has been achieved in the presence of the bacteria *Sulfolobus solfataricus* in a MBR of a different geometry.[29] The biocatalyst was incorporated in a membrane matrix made in the form of a hollow fibre consisting of a mixture of polysulphone, polyvinylpyrrolidinone, and *NN*-dimethylacetamide. An increase in the content of lyophilised cells in the mixture impaired the mechanical properties of the fibres and reduced the regularity of the membrane structure. However, these negative effects can be compensated for by varying the molecular weight of polyvinylpyrrolidinone. The study of the relation between the functional characteristics of the given MBR and their kinetic and hydrodynamic parameters showed that they can operate under both diffusional and kinetic conditions depending on the conditions specified at the inlet.

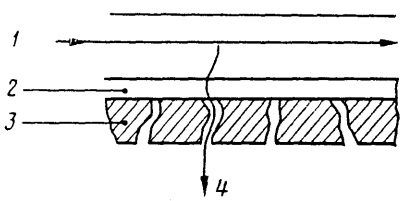


Figure 6. Schematic illustration of a flat membrane reactor with immobilised enzyme:[13] 1) substrate; 2) ultrafiltration membrane; 3) film with immobilised enzyme; 4) hydrolysate.

The microenvironment influences significantly the activity of the biocatalyst incorporated in the polymer matrix. The mechanical properties of the polymer, its biocompatibility, and its resistance to decomposition by bacteria play an important role.[30]

Membrane bioreactors in which the enzyme is immobilised as a result of the formation of cross-links or as a result of covalent attachment to the carrier surface have many advantages: they are stable, make it possible to organise the process under continuous and controlable conditions, and it is possible to obtain a uniform and relatively cheap product.[18] However, depending on the method of immobilisation, different enzymes can lose between 10 and 90% of their activity in a free state as a consequence of steric hindrance and diffusional limitations. One of the ways of overcoming the diffusional control of the chemical process in the MBR is based on the application of an asymmetric ceramic membrane.[31] Invertase is immobilised in such a membrane by filtration through a porous support and subsequent treatment with glutaraldehyde. The high

mechanical strength of the membrane makes it possible to carry out the chemical reaction under filtration conditions at pressures in the range 50–450 kPa. The contact time between the enzyme and the substrate depends on the pressure, whose variation makes it possible to regulate the rate of the reaction. The elimination of diffusional limitations ensures a significant increase in the flow of substance through the membrane.

The investigations carried out assisted in the development of a large number of a wide variety of MBR designs and demonstrated the wide scope of their uses. Among the fields in which the application of MBR may prove very effective, we may specify the preparation of ecologically pure and renewable energy carriers. The last 15 years have been characterised by a sharp increase in the employment of alcohol-containing automobile fuels which in certain countries have already acquired practical importance.[32,33] Analysis shows[32] that the coupling of fermentation with processes involving reverse osmosis, ultrafiltration, and evaporation through a membrane makes it possible to improve the economic parameters of the manufacturing process and to justify the wide-scale employment of butanol, ethanol, and acetone as fuels. The designs of various membrane fermenters,[34,35] including those for the synthesis of ethanol,[18] are being vigorously developed.

Methane and molecular hydrogen are believed to be a promising basis for future power engineering. One of the possible ways of obtaining H_2 – via the photodecomposition of hydrogen sulphide – was mentioned previously. An alternative approach is based on the fact that hydrogen and methane are the products of a large number of micro-organisms,[33,36,37] including phototropic micro-organisms for which light serves as the energy source. Hydrogen can be evolved both by whole cells and by isolated polyenzyme systems containing hydrogenases,[38] the activity of the hydrogenases exceeding appreciably the activity of the catalysts based on platinum group metals and persisting for a long time at a high level (the half-inactivaion period is about 60 days[39]). Thus the creation of fermenters for the manufacture of hydrogen and methane in which the principles of MBR would be realised (see, for example, Fig.5) is of undoubted interest for the solution of energy problems. The survey of modern concepts in the design of MBR for plant cells has been published.[40] A favourable factor for the development of hydrogenase-containing MBR is also the fact that, when hydrogenases are incorporated in lipid liposomes (a procedure used for the immobiliisation of biocatalysts on synthetic membranes[41]), an increase not only in the stability but also in the activity of the enzyme is observed in a number of instances.[42]

3. Organised Molecular Assemblies

Organised molecular assemblies – structures formed spontaneously by amphiphilic molecules in aqueous solutions – are of considerable interest for the development of integrated membrane systems. The simplest organised molecular assemblies are monolayers on interfaces, and micelles, microemulsions, double layers, and vesicles.[43] The tendency towards self-organisation by lipid molecules in the form of a double layer determines the principal structural features of biological membranes. Liposomes, closed double layer lipid membranes containing an internal aqueous phase with dimensions in the range 20–500 nm, as well as molecular monolayers have attracted most attention. The use of liposomes to carry out chemical reactions is determined by the following main factors.[41,43] Firstly, in the inner volume and in the walls of the liposome, the test substances are present at relatively high concentrations. Secondly, the formation of liposomes is accompanied by the creation of a surface with an extremely large area. For example, at a lipid concentration of 4 mg ml^{-1}, the area of liposomal membranes is ~ 1 m^2 ml^{-1}. Thirdly, liposomal membranes are characterised by a high permeability to non-electrolytes (10^{-4}–10^{-6} cm^3 cm^{-1} s^{-1}) and a low permeability to hydrophilic molecules (10^{-9}–10^{-10} cm^3 cm^{-1} s^{-1}). A liposome containing in the inner aqueous phase some kind of enzyme is in essence a membrane microreactor constructed at the molecular level.[44] Liposomes can be used in MBR for the soft immobilsation of enzymes:[41] initially the enzyme is built into the liposomal membrane, where it is incorporated in the inner aqueous phase, and the liposomes are then immobilised on a porous membrane. The stability of the immobilised liposomes is higher compared with the free liposomes. Another way of increasing stability consists in creating around the vesicle a polymer shell chemically bound to the outer surface of the membrane.[45] The vesicles, which are stable in the course of several months, can be prepared from molecules with double bonds which undergo polymerisation after the formation of the vesicles.[43]

Microcapsules, which are analogous to polymeric vesicles but are larger, have been investigated as "containers" for biocatalysts in pioneering investigations.[46,47] Microcapsules having diameters ranging from 1 to 100 μm have been obtained by interfacial polycondensation, aqueous solutions of the enzymes being emulsified in an organic phase. A solution of the enzyme, whole cells, or their fragments were enclosed in nylon or collodion capsules, no appreciable leakage of the protein from the capsules being observed in the course of approximately a week. The membranes of the capsules are permeable to low-molecular-weight substrates and products, their transport taking place by means of diffusion via water pores ~ 1.6 nm in diameter, and in the most successful specimens the activity of the enzyme, measured as the rate of accumulation of the product, approaches the activity in the native state.[46] The possibility of using microcapsules in biochemical studies *in vitro* and also for therapeutic purposes *in vivo* has been studied. One of the significant limitations in the use of systems of this kind consists in the risk of the denaturation of the protein in interfacial polymerisation in the course of the formation of the microcapsule. Earlier studies on the encapsulation of enzymes served as a basis for the development of the first MBR containing the biocatalyst within hollow fibres.[22]

The development of studies on microencapsulation led to the creation of systems in which interfacial catalytic reactions can be carried out at a liquid/liquid interface. The enzyme is immobilised on the outer surface of a porous nylon capsule filled with an aqueous buffer solution,[48] which is placed in the organic phase (Fig.7). The synthesis of peptides takes place at the interface between the aqueous phase and chloroform, the enzyme being protected from the inactivating effect of the organic solvent by a surface layer of buffer solution seeping through. In contrast to the traditional capsule MBR, in this bioreactor, the molecular weights of the starting materials and products need not necessarily be low. Other advantages of the system are the simplicity of the separation of the biocatalyst from the substrate and product and also the absence of an induction period in the catalytic reaction associated with swelling processes.[48]

The use of an organised assembly of molecules in the form of a monolayer at the interface ensures major technological possibilities. The method of depositing monomolecular layers on the surface of a solid support proposed by Langmuir constitutes nowadays the basis of numerous developments in the field of microelectronics, optics, and electro-optics and for the creation of photoelectric converters and information processing systems.[49] The introduction of methods

for the preparation of ultrathin layers into membrane technology makes it possible to outline new approaches to the creation of integrated systems.[50] In the first place, one should note the possibility of obtaining infinitesimally thin composite membranes which could be used to devise highly productive MBR. The high degree of order in the molecular arrangement in the monolayer makes it possible to carry out chemical reactions under unusual conditions where highly specific effects can be manifested. The successive deposition of different monolayers permits the creation of mixed structures whose properties can be controlled at the molecular level with attainment of maximum integration. The introduction of suitable functional components into a thin layer system renders them sensitive to chemical, electrical, or optical signals, which can be used to control properties of the deposited film. In such systems, one can achieve not only material transfer but also transfer of information. Thus the study of integrated membrane systems requires the expansion of traditional ideas about the membrane as a passive selectively permeable partition, because in systems of this kind it can play the role of an active element acting on the chemical state of the given substance (membrane reactors) or participating in the generation and transformation of signals (membrane sensors).

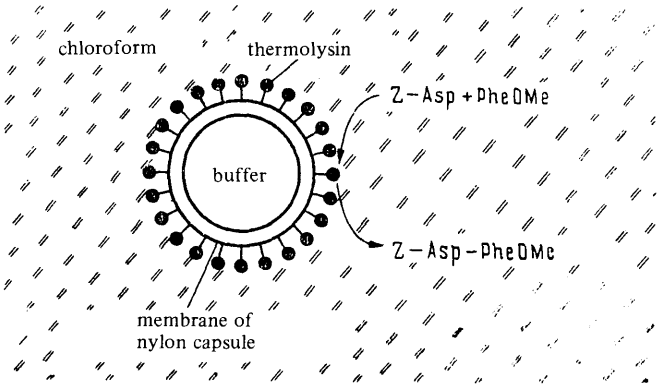


Figure 7. Design for a capsule membrane bioreactor for the synthesis of peptides.[48]

We shall deal briefly with certain examples of the use of thin-layer membrane systems. A method has been proposed for the formation of a thin-layer membrane from fragments of cell walls of certain bacteria.[51] The immobilisation of glycoprotein fragments having pores of uniform size 2–6 nm in diameter on the surface of a porous synthetic support makes it possible to use the resulting membrane for ultrafiltration in the pH range from 1 to 13.

Studies on processes involving the photoinitiated intramolecular electron transport in ordered donor–sensitiser–acceptor systems, formed by the Langmuir–Blodgett method, showed that it is possible to achieve states with separated charges on a nanosecond time scale.[50] A system functioning as a photodiode has been obtained by depositing on a gold electrode monomolecular films containing bound residues of viologen, pyrene, and ferrocene.[52]

Thin-layer membranes have found extensive applications as sensitive elements in chemical sensors for biomedical research and for the control of processes in bioreactors *in situ*.[53] One of the ways of creating sensor devices consists in the use of the structure of a semiconducting field transistor as the base for the deposition of a membrane exhibiting a specific chemical sensitivity.[53–55] Planar silicon transistors with an oxide or nitride dielectric film are usually employed, the immobilised enzyme being deposited on the region of the transistor gate. The change in the electrical potential at the gate as consequence of the chemical interaction with the substrate modulates the state of the conducting channel, which is recorded by electrical methods. This principle has been used to create biosensors sensitive to glucose, ATP, glutamic acid, urea, and other organic compounds.[53–55] Biosensors of this type have many undoubted advantages: they can be miniaturised, are readily "integrated" in technological schemes, make it possible to combine various sensors in a single semiconductor crystal, have good metrological characteristics, and there exists a sophisticated technology for their preparation. The use of enzymes in biosensors ensures the possibility of recording a broad spectrum of substances with an enormous sensitivity (the concentration of the substances detected can be as low as 10^{-19} M).[56] The use of thin-layer membranes in sensor devices is justified by the fact that the response time of the sensor is inversely proportional to the square of the thickness of the sensing membrane and can amount to several seconds.[54]

Membranes based on double-layer and multilayer molecular structures have been used successfully for the highly selective determination of anions and cations by electrochemical[57,58] and spectroscopic[59] methods. A monomolecular lipid layer at the water/air interface has been investigated as a model of the olfactory membrane.[60] The absorption of a gaseous component (diethyl ether) or its incorporation in the lipid monolayer increases sharply the permeability of the film to water vapour.

Photo- or chemo-sensitivity of the membranes can be used not only for the creation of recording systems but also for the active regulation of the functional properties of membranes in integrated systems. The possibility of a controlling effect on the components of complex membrane systems greatly extends the number of independent operational variables and permits the realisation of new operating conditions and an increase in the flexibility of such systems, for example, membrane bioreactors.

One of the biological objects having a wide set of functional properties which can find technical applications is the membrane protein complex bacteriorhodopsin. The principal properties of bacteriorhodopsin and the possibilities for its employment in membrane systems are considered below.

III. FUNCTIONAL PROPERTIES OF BACTERIORHODOPSIN IN ARTIFICIAL SYSTEMS

1. Purple Membranes Containing Bateriorhodopsin

It is well known that lipid membranes play a key role in the processes involving the transformation of energy by living cells. In the highly specialised biological membranes effecting fundamental processes such as respiration or photosynthesis, the multienzyme complexes bound to the membrane catalyse a whole chain of coupled electron- and proton-transfer reactions in the course of which chemical energy is stored.[61]

Recently the so called purple membranes (PM), synthesised by the bacteria *Halobacterium halobium*, have attracted the attention of investigators. In these comparatively simple but highly specialised

membranes, a vector transmembrane transfer of H^+ takes place under the influence of light.[62]

The purple membranes from *H. halobium* consist to the extent of ~75% of a single protein—bacteriorhodopsin (Br),[62] while the remaining 25% comprises acid lipids.[63] Bacteriorhodopsin is a single chain protein consisting of 248 aminoacid residues[64,65] and having a molecular weight of ~26.5 kDa. The chromophoric group of the protein is the aldimine of retinal, which is bound covalently to the ε-amino-group of lysine, forming a Schiff base.[62]

The X-ray low-angle and diffraction methods[66] as well as limited proteolysis and immunochemical binding to monoclonal antibody experiments[67] have shown that the polypeptide chain of the Br molecule has seven α-helical transmembrane strands connected by protein sections exposed to the aqueous phase on the surface of the membrane. According to electron microscope data, the Br molecules in the plane of the membrane form a dense hexagonal quasi-crystalline lattice,[68] whose main structural element is Br trimers (Fig.8).

The Br in the membrane can exist in two stable forms—the dark-adapted and light-adapted forms between which transitions are possible. In the light-adapted Br, the retinal is in the fully *trans*-conformation, while the dark-adapted Br is an equimolar mixture of 13-*cis*- and fully *trans*-isomers.[69] Both 13-*cis*-Br and the fully *trans*-Br are photochemically active and are characterised by cycles of photochemical transformations.

The photochemical cycle of the light-adapted fully *trans*-Br has been studied in fair detail from the primary sub-picosecond stages. During the cycle, deprotonation and subsequent reprotonation of the Schiff base and the isomerisation of retinal with respect to the C(13)=C(14) double bond take place. During the photocycle, the fully *trans*-Br passes through at least six metastable states—the intermediates J, K, L, M, N, and O, whose lifetimes are in the range 0.4 ps–(5–10) ms (see the relevant reviews[70,71]).

Very much less is known about the photocycle of 13-*cis*-Br, for which three intermediates have been postulated: ^{x}C, ^{y}C, and ^{610}C (610 nm is the maximum of the optical absorption of the intermediate). In the ^{y}C state the photocycle branches and there is a probability of the transition of Br to the fully *trans*-form.[72]

The nature of the primary intermediate in the photocycle has continuously attracted the attention of investigators, because this is in fact the site where energy is stored and is subsequently used for the transmembrane transfer of H^+.

It has been established with the aid of pulse laser absorption and fluorescence spectroscopy with sub-picosecond time resolution that, after the absorption of a light quantum, the light-adapted Br passes to a singlet excited state, whose lifetime is τ = 0.4–0.7 ps.[73] The rate of relaxation of the excited state is the same as the rate of formation of the intermediate J, the absorption spectrum of which has undergone a bathochromic shift of ~30 nm relative to the Br spectrum. The intermediate J is converted in its turn over a period = 5 ps into the intermediate K whose absorption spectrum has undergone a bathochromic shift of 20 nm relative to the Br spectrum.[73,74] The lifetime of the intermediate K is 1–2 μs and is the same as the time required for the formation of the photocycle intermediate having an absorption maximum near 550 nm (L_{550}). In this and preceding stages, the albumin of the retinal in Br is in the protonated state.

The next stage in the cycle of photochemical transformations of Br is the transition from the intermediate L_{550} to one of the functionally most important forms, namely M_{412}, which corresponds to the deprotonated state of the Schiff base of retinal. The intermediate M_{412} is formed ~40 μs after the absorption of a photon. The formation of the M_{412} photoproduct can be recorded by low-temperature or pulse absorption spectroscopy at the absorption band near 410 nm and also from the appearance of the 1570 cm^{-1} band due to the C=C stretching vibrations in the kinetic resonance Raman spectra.

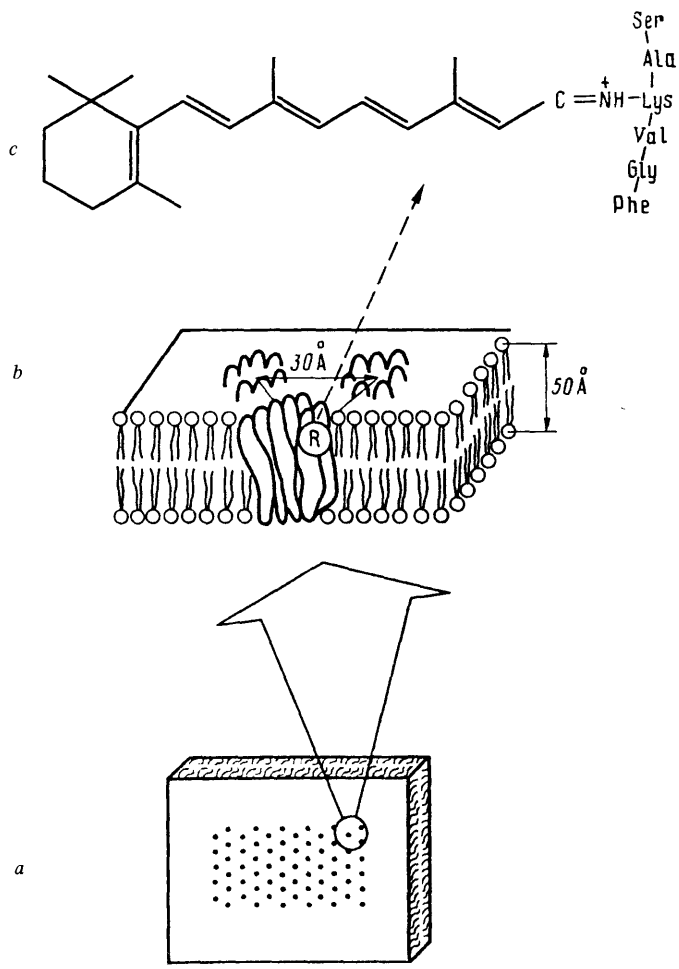


Figure 8. The structure of purple membranes containing bacteriorhodopsin:[68] *a*) fragment of the purple membrane, the dots denoting the molecules of bacteriorhodopsin forming a quasi-crystalline structure; *b*) bacteriorhodopsin trimer; *c*) chromophoric group of bacteriorhodopsin—retinal, bound as a Schiff base with Lys-216 of the polypeptide chain of bacteriorhodopsin.

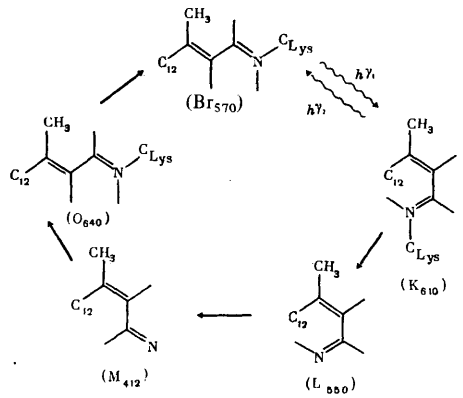
The process leading to the formation of the M_{412} form is one of the key stages in the functioning of Br as a light-dependent proton pump. The most significant changes in the ionic state of a number of aromatic aminoacid residues and carboxy-groups of the protein

have been recorded in the stages involving the formation and decomposition of the M_{412} intermediate. It has been established that a proton is split-off from the Schiff base and H+ is transferred through the membrane at this stage.

Approximately 10 ns after the formation of the M_{412} intermediate, the regeneration of the initial form Br_{570} is observed. As a rule, this transition is described by the following sequence of photoreactions: $M_{412} \rightarrow (N_{520}) \rightarrow O_{640} \rightarrow Br_{570}$ (the N_{520} intermediate is enclosed in brackets because many workers have failed to confirm its existence). The application of pulse Raman spectroscopy with picosecond time resolution made it possible to investigate the dynamics of the conformational changes in retinal. In the range 1100–1400 cm^{-1}, the Raman spectra of 13-*cis*-Br and fully *trans*-Br differ significantly. The Raman spectrum recorded several picoseconds after the application of the laser flash to the light-adapted (fully *trans*-Br) specimen resembles very closely the spectrum of 13-*cis*-Br. When the medium with H_2O is replaced by one with D_2O, an analogous spectral correspondence is observed between the "picosecond intermediate" and 13-*cis*-Br but in a somewhat different wavelength range (950–1050 cm^{-1}). The band corresponding to the -C=NH bond of the Schiff base (1646 cm^{-1}) in the picosecond time range is broadened and undergoes a shift, which may indicate a change in the electronic structure and in the direct environment of the -C=NH groups.[75,76]

Quantum-chemical analysis of the vibrational spectra with retinal-deuteriated or ^{13}C-modified in the C(15)-position, recorded by Fourier-transformation IR spectroscopy, as well as the resonance Raman spectra of the analogous Br preparations with biosynthetically ^{13}C-modified retinal have shown that the following changes in the chromophore structure take place: Br_{570} (fully *trans*) → K(13, 14-*s*-*cis*) → L(13, 14-*s*-*cis*) → M(13-*cis*) → O(fully *trans*).[77,78]

The cycle of photochemical transformations of the light-adapted Br and the structural rearrangments of retinal near the Schiff base are illustrated in the scheme below:



2. Photoelectric Processes

In the course of the photochemical reactions of Br, protons are transferred from the intracellular volume through the membrane to the outer medium, which creates a gradient of the electrochemical potential of hydrogen ions on the cell membrane. The energy stored in the form of the difference between the electrochemical potentials is used for the synthesis of ATP, membrane transport, the motion of the bacterial cell, metabolic processes, etc. The exact mechanism of the active proton transport in Br has not been established. The energetic, structural, and kinetic aspects of the functioning of the proton channel have been discussed in the literature.[79,80]

The direct experimental measurement of the photoelectric activity of Br[81,82] is based on the retention of its functional properties when it is incorporated in artificial phospholipid membranes, liposomes, or phospholipid-impregnated membrane filters separating electrolyte solutions. The action of light induces the transfer of H^+ between the membrane-separated sections and creates an electrical potential difference, which can be measured with the aid of reversible electrodes or potential-sensitive probes.

The use of a low-inertia recording system as well as pulse laser excitation permits an increase in the time resolution of the method of measurement of the photopotential down to microseconds[83] and picoseconds.[84,85] The processes involving an increase and fall in the photopotential generated by Br have several phases correlated to a first approximation with the formation and decomposition of the intermediates K, L, and M in the Br photocycle.[83] It has been suggested that the generation of photopotential in such systems is associated with the intramembrane displacement of charged groups (displacement currents) and the transmembrane H^+ transport.

Model systems containing Br as part of the composition of artificial lipid membranes can consist of liposomes or planar macroscopic membranes. It has been shown with the aid of potential-sensitive dyes that a photopotential up to 200 mV arises on the membrane in artificial lipid vesicles under stationary conditions.[86] In the liposomes, the direction of proton transport can be the same as the direction of transport in cells or can be opposed to it[87] depending on the method of preparation of the liposomes, the type of lipids used, and the pH of the medium.[88,89]

The Br in liposomes can be incorported as a single protein component or in combination with other membrane proteins, such as ATPase, cytochrome oxidase, and other enzymes of the respiratory chain.[87,90–93] In the last case, the membrane electrochemical potential, generated by Br on illuminaion, can provide the energy for phosphorylation processes and can exert a regulatory effect on the activity of enzymes. The organised molecular assemblies obtained when Br and other enzymes are incorporated in double layer lipid membranes make it possible to achieve functional coupling between proteins, the monomeric Br serving as a more effective source of energy than the native purple membranes by virtue of the closer packing of the monomer in the liposome.[94]

Br is capable of being sorbed at the octane/water interface and, under illumination in the presence of an electron acceptor in the octane phase, a potential difference up to 0.5 V is generated between the phases.[95] When ATPase is introduced into such a system, photophosphorylation can take place in the latter.

The photoelectric activity of Br in planar double-layer ("black") lipid membranes was first demonstrated in two studies.[96,97] It was established that the photopotential of 100–180 mV, arising when the system is illuminated with light at a wavelength of ~560 nm (the Br absorption maximum), diminishes to zero under the influence of blue light absorbed by the intermediate M driving the photocycle. An analogous regulation of the photoelectric properties of Br by light having different spectral composition occurs also in other model systems.

The principal disadvantage of planar double layer lipid membranes is their low stability. The addition of fillers to solutions from which the membranes are formed makes it possible to increase severalfold the lifetime of the membrane and the breakdown potential.[98] Even more stable systems are obtained when Br is sorbed on lipid-impregnated porous filters or collodion membranes.[99]

The photoelectric activity of Br immobilised in polyacrylamide gel has been recorded in a number of studies.[100,101] The kinetic characteristics of the photoelectric signals indicate that Br remains intact on polymerisation of the gel.

Br or purple membranes can be immobilised in other polymer matrices [poly(vinyl alcohol), gelatin]. Such dry membranes with additives modifying the spectroscopic and kinetic properties of Br have come to be called "Biokhrom" films. They constitute a promising photochromic material for the reverse optical recording of information.[102]

The immobilisation of Br increases the stability of this protein, which is high even in the absence of this step and is unique for biological systems. Thus Br retains its photochemical activity over a wide temperature range (from helium temperatures to ~370 K), a wide pH range (3–10), and a wide range of ionic strengths of the solution (from distilled water to saturated NaCl solution) and exhibits a high resistance to the action of proteolytic enzymes[67,103] and certain organic solvents and detergents.[104] The "Biokhrom" films or dry films prepared from purple membranes retain their funcional activity for many months and even years and withstand without loss of activity up to 10^7 "light–dark" switching cycles. For certain applications, such "solid state" systems, obtained by immobilising and drying Br on solid supports, are in fact most promising. The functioning of Br in dry membranes has a number of characteristic features compared with its functioning in the whole cell or in an aqueous suspension of purple membranes.

3. Characteristics of the Photochemical Reactions of Bacteriorhodopsin in Dry Membranes.

Br retains its capacity for reversible photochemical reacions under the conditions of partial dehydration, the reaction cycle in fairly moist films ($\gtrsim$60%) being virtually the same as in an aqueous suspension.[105,106] The formation and decomposition of the intermediate M, i.e. deprotonation and protonation of the chromophoric group of Br in the absence of water as the liquid phase, show that these processes apparently proceed in the cell with participation of endogenic proton donors and acceptors, which are probably the aminoacids tyrosine and aspartic acid localised in the vicinity of the Schiff base.[80,105]

Together with the similarity of the photochemical processes occurring in suspension and in dry purple membrane preparations, certain significant differences are observed between them: (1) for a low humidity, the position of the maximum in the absorption spectrum of multilayer purple membrane films undergoes a hypsochromic shift of 5–10 nm compared with the maximum in the spectrum of the suspension.[107] (2) The dark and light adaptation in multilayer purple membrane films of a relative humidity < 100% differs from the adaptation in the purple membrane suspension.[107,108] In the films which are in the light-adapted state, the ratio between the Br isomers with 13-*cis*-retinal and the fully *trans*-retinal depends on the wavelength of the exciting light and on the humidity. (3) Together with the photochemical reactions of fully *trans*-Pr in dry purple membrane preparations, photoreactions of 13-*cis*-Pr, from the photocycle of which the deprotonated intermediate M is absent, are observed. (4) The photochemical cycle of the fully *trans*-Br in dry membranes is reduced compared with the photocycle in an aqueous suspension – the intermediates L and O are absent[106,109,110] while in moist membranes the characteristics of the Br cycle approach those of the photocycle in cells.[111]

After extensive dehydration of the purple membrane, the absorption maximum of Br shifts from 570 to 530 nm.[112] According to Raman spectroscopic data, in the new state aldimine is in the deprotonated form, while retinal is predominantly in the 13-*cis*-configuration. Under illumination, the dehydrated Br_{530} undergoes a photochemical reaction cycle with the following stages: the formation of a batho-intermediate with a spectral maximum at 630 nm, the formation of an intermediate with a maximum at 412 nm (formation time τ = 2.5 ms), and relaxation of the latter over a period τ = 2 s to the initial form Br_{530}.

Apart from the features of the photocycle indicated above, in dry films one can also note an increase in the lifetime of the intermediate M, which amounts to several seconds and even several tens of seconds at room temperature[109,110,113] compared with several milliseconds in an aqueous suspension. The lifetime of the state M increases also after the addition of glycerol to aqueous solutions of purple membranes.[114,115]

Methods for the preparation of oriented films or membranes containing purple membranes as the working element have been developed for a more far-reaching study and more complete utilisation of the molecular photochromic and photoelectric properties of Br.

4. Methods for the Preparation of Oriented Films of Purple Membranes and the Photoelectric Properties of Such Films

Various procedures for orienting purple membranes have been described: by the centrifugation method,[116] at the air/water interface as a result of hydrophobic interactions,[117] in a magnetic field as a consequence of the anisotropy of the diamagnetic susceptibility of the protein segments,[118] on charged surfaces modified with polylysine,[119] in the electric field of an air condenser,[105] and in an electric field applied directly to the suspension.[120] Chemical cross-linking has also been used to orient the purple membranes and to stabilise the resulting structure.[121]

The orienting of purple membranes in a magnetic field[118] is based on the diamagnetic properties of the α-helical structure of the protein, which is the preferred form of organisation of the Br molecules. Exposure of a purple membrane suspension to the action of a magnetic field results in the appearance in the former of a certain degree of order which can be fixed by drying.

Oriented purple membrane films have been obtained by the deposition onto a support of monolayers formed by the Langmuir–Blodgett method.[117,122] The study of the state of the purple membrane monolayers in a mixture of purple membranes with aliphatic acids at the air/water interface made it possible to determine their dynamic characteristics and to confirm the possibility of the formation of multilayers by the Langmuir–Blodgett method.[123] Membrane systems consisting of oriented molecular purple layers, obtained by the Langmuir–Blodgett method and deposited on a thin Teflon support or another neutral carrier, have been regarded by some workers as prototypes for molecular computing elements.[124,125] This system is fairly readily available and sufficiently stable to be able to carry out rigorous quantitative measurments and at the same time the molecular organisation of the purple membrane is fairly complex, which creates a basis for the modification of its structure bv controlling the photosignal.

Multilayer films, within which the purple membranes are arranged rigorously parallel to the plane of the support, can be obtained by centrifugation and sedimentation methods.[116] However, in this procedure for the formation of the film, the purple membranes can be oriented with equal probability with both its cytoplasmic and

periplasmic surface directed towards the support. The preparations obtained are distinguished by a high degree of purple membrane packing order, but the direction of the photoinduced H^+ transport in each membrane is selected at random out of the two possible directions.

A similar ordering of the film can be achieved by drying a purple membrane suspension on a glass, mylar, or mica plate. In this case, the purple membranes are spontaneously "arranged" in the plane of the suport by virtue of the much greater diameter of the purple membrane compared with its thickness (about 300 and 5 nm respectively). However, in such spontaneous sedimentation, bending of the purple membrane discs and other distortions in their structure may be observed.

The methods for orienting purple membranes based on the different properties of the cyto- and peri-plasmatic surfaces are of considerable interest. Purple membranes have a large permanent dipole moment due to the different surface charge densities on the opposite sides of the membrane. The dipole moment is ~ 140 D at pH 7.[126] The freezing of the purple membrane suspension in an external electric field makes it possible to create and fix a preferred orientation of the purple membrane relative to the applied electric field vector.[127]

In order to obtain preparations of oriented purple membranes, drops of a suspension deposited on an electrically conducting support and dried in a permanent electric field have also been used.[105] However, since the drying was carried out in the field of an air condenser, the appreciable difference between the dielectric constants of air and the purple membrane suspension precluded the attainment of an appreciable electric field strength within the suspension and, furthermore, the field inside the drop was significantly inhomogeneous. A high degree of order was not therefore attained in the purple membranes in preparations obtained by the above method.

An appreciably greater order was achieved using the electrophoretic method for the deposition of purple membranes on a flat electrode.[120] In this case, the electric field is applied directly to a deionised purple membrane suspension. It is known that purple membranes contain acid lipids,[63] which are negatively charged in a neutral medium. For this reason, purple platelets exhibit an electrophoretic mobility and at a pH of about 7 the purple membranes move towards the anode.

Analysis of the methods enumerated shows that the electrophoretic deposition and subsequent drying of purple membranes on an electrically conducting support make it possible to obtain preparations in which the Br platelets are ordered to the maximum extent. Under the influence of light, such highly oriented membrane structures generate an electric potential up to 10–11 V (for a thickness of the specimen of about 10 μm [128]). The photoelectric signal generated by Br consists of two components: the displacement current associated with the redistribution of charges within the membrane and the constant photocurrent induced by the transmembrane proton transport and coupled with electrochemical reactions on the surfaces of the electrodes.[129]

The appreciable value of the photosignal and the compactness of the system, tending to decrease parasitic electrical capacitances, made it possible to record by means of the picosecond laser technique the increase in the photoelectric signal, whose front proved to be shorter than 5 ps,[84] and also to create on the basis of purple membranes the first biological photodiode having the picosecond time resolution.[85]

An important property of the Br-containing membranes is the dependence of the spectroscopic and photoelectric characteristics on the applied external electric field, which creates a basis for controlling membrane systems.[71,130]

5. The Use of Bacteriorhodopsin in Membrane Reactors

The use of external influences for regulating the conditions in the operation of MBR reflects the tendency towards the organisation of processes in accordance with the principles applied in biological systems. Flexible rearrangeable systems apparently exhibit greater potential possibilities for their optimisation. The study of photochemical reactions in polymer films as a possible way of regulating the properties of membranes is of undoubted interest. Photosensitive polypeptide membranes can be prepared from poly-L-glutamic acid containing chromophoric *para*-rosaniline groups.[131] On irradiation with UV light, photodissociation, accompanied by the conformational transition of the polypeptide to the α-helical structure, takes place. In the dark, the structure relaxes to the initial structure and the process is thermally activated. Since the transport properties of the membrane depend on the conformational state of the polypeptide,[132] illumination can be used as a way of altering the permeability of the membrane. Apart from photodissociation, a further two photochemical processes, leading to a significant alteration of the properties of the molecules forming thin membranes, are known: *cis–trans* isomerisation and reactions involving a change in the hydrophilic properties of the head groups of amphiphiles. Photoreactions of the latter type have been investigated in multilayers of photosensitive amphiphilic molecules formed by the Langmuir–Blodgett method.[133] When the films are illuminated with near UV light, their permeability to ions diminishes, which has been attributed to the formation of a more compact film structure. The transition of the membrane to a non-conducting state is photoreversible, relaxation ocurring under the influence of visible light. Thus the system behaves as an ionic phototrigger: the absorption of small radiation doses induces a fairly appreciable change in the electric current. An interesting feature of the compounds examined is that, in relation to Br, they can play the role of a photoinhibitor, because the region corresponding to absorption by the induced UV-irradiated form of the substance overlaps the absorption band of Br.[133]

The permeability of synthetic polyvinyl polypeptide copolymer membranes, which form polypeptide microdomains, depends significantly on the pH of the medium,[134] which determines the conformational state of the polypeptide sections. For an appropriate choice of geometry and also of the method of immobilisation of the pigment, one can apparently make use of the proton transport function of Br to influence processes involving the transport of organic substrates through the membranes considered. Probably other enzymes catalysing reactions with participation of H^+ can also be regarded as possible regulators of the pH-dependent properties of synthetic membranes. Oxidation-reduction processes also influence the properties of certain membranes, for example, poly-L-cysteine membranes.[135]

The permeability of multilamellar membranes formed from amphiphiles of the liquid crystal type is a function of the electric field applied to the membrane.[136] Depending on the chemical composition of the membrane, its permeability depends either on the lateral or the transmembrane electric field. In the latter case, the photoelectric activity of Br can apparently be used to regulate the permeability of liquid crystal films.

The electric potential influences not only the passive processes involving the permeation of substances through the membrane but in certain cases determines also the activity of the biocatalyst. Thus an appreciable increase in the activity of alcohol dehydrogenase, immobilised on an electrically conducting polypyrrole membrane, with increase in the potential applied to the support has been observed.[137] The increase in enzyme activity has been attributed to

the overcoming of the diffusional restrictions for products and substrates as a consequence of the change in the overall charge on the membrane matrix. Presumably the use of Br, which possesses electrogenic properties, in systems of this type is extremely effective, because the application to the membrane of a potential of 0.7 V increased by a factor greater than 10 the activity of the enzyme.[137] Photopotentials of this magnitude can be comparatively readily obtained using oriented Br preparations. In order to regulate the photoactivity of KBr itself, it has been suggested that cationic amphiphiles, capable of forming double layers in the aqueous phase, be used.[138] These substances form bonds with the negatively charged groups on the purple membrane surface, which blocks the processes involving proton capture from the medium by Br. Another approach to the regulation of the properties of Br is associated with the development of gene engineering. The methods of gene engineering made it possible to obtain Br analogues in the molecules of which individual aminoacid residues have been replaced by others.[139] Hitherto 14 such mutants, whose proton transport activity and spectroscopic activities are different to those of native Br, have been obtained.

Thus a wide variety of types of membrane bioreactors, which are capable of being constructed and are suitable for carrying out a large number of industrially important processes with effective economical parameters, have been developed. Presumably a more far reaching recourse to the principles of the organisation of processes in biological systems will prove extremely useful for further development of MBr. The creation of more flexible and effective integrated membrane systems may be promoted by the employment of regulatable elements whose properties change under the influence of chemical substances, light, electric or magnetic fields, and also other types of influence. It appears of interest to investigate highly non-equilibrium MBR operating conditions under which spatial-time oscillations arise in the concentrations and fluxes of the components. A far-reaching modulation of properties can be obtained in hybrid systems incorporating particular biological complexes and funcional polymer membranes. In such systems, it is possible to control the mineralistaion of the working volumes and to normalise the supply of substrates as a result of the symport or antiport of the components transferred by the transport proteins. Br, which has extensive functional possibilities and an exceptionally high stability, is a convenient object for use in control elements. In ordered molecular assemblies, Br can play the role of a rapidly acting photoelectric and photoelectrochemical converter. The simplicity and susceptibility to technological formulation of the preparation of Br-containing membrane systems creates preconditions for their practical use. The study of the possible application in hybrid systems, apart from Br, of other energy-dependent biological complexes—the reaction centres of photosynthesising systems, transport ATPases, etc.—is also of undoubted interest.

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Relaxation and Two-dimensional Phase Transitions in the Electrical Double Layer

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The excess entropy of formation and the characteristic relaxation times of the electrical double layer at the interface between the metal and electrolyte solution have been determined by the laser temperature jump method, consisting in the measurements of the electrical signal of an electrochemical cell on heating a metallic electrode by nanosecond laser pulses. The combination of the laser temperature jump data and data obtained by electrochemical methods shows that the orientational rearrangement of the solvent monolayer and the adsorption of surfactants occurring when the electrode potential and the solution composition are altered have the character of two-dimensional first- and second-order phase transitions.
The bibliography includes 73 references.

CONTENTS

I.	Introduction	605
II.	Pulse heating of the metallic electrode	606
III.	Temperature coefficients of the potential drop in the electrical double layer	607
IV.	Methods of measurement	608
V.	The laser temperature jump in dilute electrolyte solutions	609
VI.	The excess entropy and heat capacity of the dense part of the electrical double layer	610
VII.	Adsorption of anions	612
VIII.	Adsorption of organic substances	614

I. INTRODUCTION

Data obtained by classical electrochemical surface tension and differential capacitance methods serve as the experimental basis for the electrochemical double layer (EDL) theory. Their measurement at the interfaces beween electrolyte solutions and ideally polarisable metallic electrodes with atomically smooth surfaces, in particular, the mercury electrode, has ensured a quantitative descriptiion of the principal phenomena: the formation of surface excess amounts of ions in the dense and diffuse parts of the EDL and the adsorption in its inner part of dipolar solvent molecules, ions, and surfactants (see, for example, Frumkin[1] and Delahay[2]). However, in connection with the development of theoretical models of the EDL, for the testing of which it is necessary to have data on its structure and dynamic properties, it was discovered that these traditional methods have limitations. The study of the packing and orientation of the molecules and of the interactions between them, of the molecular mobility in the interface, of the change in the degree of hydration of the ions on passing from the bulk of the solution to the EDL, and of a multiplicity of similar questions stimulated the creation of new

methods. One of these is the method of the laser temperature jump (LTJ) in which the temperature coefficients of the decrease in the potential and the characteristic relaxation times of the EDL are measured. The first of these quantities is thermodynamic and in this respect the LTJ method supplements the traditional electrochemical methods. The dependences of the relaxation times on the electrode potential and the solution composition, first measured with the aid of the LTJ method, revealed a relation between the dynamics of the EDL and its structure.

The first studies of the EDL by this method were closely related to the investigation of photoemission from metals into electrolyte solutions.[3] In one of the first studies of the characteristics of the photoemission,[4] it was observed that the change in the potential of the electrode following its pulse illumination is caused not only by the emission of electrons from the metal into the solution but also by the heating of the electrode by the light absorbed in it. The pulse heating signal γ_h was separated from the photoemission signal using light at a sufficiently long wavelength for which there is no photoemission. According to Korshunov et al.,[4] γ_h exhibits a characteristic dependence on the electrode potential E and, in particular, it changes sign near the zero-change potential (ZCP). Barker and Cloke,[5] who studied the $\gamma_h(E)$ relation in greater detail, observed a shift of the zero response potential (ZRP), at which $\gamma_h = 0$, relative to the ZCP, amounting to between −0.10 to −0.15 V and being caused by the dipole potential jump. At the ZRP, the water dipoles in the inner part of the EDL undergo reorientation. Barker and Cloke[5] studied the $\gamma_h(E)$ relations in acid solutions and showed that γ_h has a constant component due to thermal diffusion.

In the first investigations,[4,5] the electrode was heated by light pulses with a duration $t_0 \gtrsim 10^6$ s, whereupon the kinetics of the heating signal are determined by the form of the pulse and the time constant of the electrochemical cell. Measurements have been made[6] of $\gamma_h(E, t)$ on laser heating ($t_0 \cong 10^{-8}$ s), which showed that in dilute electrolyte solutions in the vicinity of the ZCP, the relaxation time of the diffuse part of the EDL corresponds to the time of the diffusional displacement of ions by the Debye length, while the relaxation time of the dense part of the EDL increases sharply over a wide range of potentials close to ZRP.

It has been shown[7] that the heating signal is proportional to the derivative of the excess entropy of the EDL S^σ with respect to the charge of the electrode, i.e. S^σ has an extremum at the ZRP. In the range of potentials corresponding to the ideal polarisability of the mercury electrode, three ZRP, corresponding to two maxima and a minimum in S^σ maxima, the sharp increase in the relaxation times in their vicinity, and also the anomalies in the excess heat capacity calculated from the temperature variations of S^σ justify the hypothesis that the orientational rearrangement of the monolayer of water dipoles in the inner part of the EDL, occurring under the influence of its electric field, is a two-dimensional second-order phase transitions.[8,9]

Further investigations by the LTJ method demonstrated that the $\gamma_h(E)$ and $\tau(E)$ relations are extremely sensitive to the change in the structure of the EDL associated with the adsorption of inorganic anions and surface-active organic substances.

The question of two-dimensional phase transitions was raised in one of the first communications by Frumkin,[10] who stated that, in the presence of a strong intermolecular attraction of the adsorbed organic molecules, the adsorption layer becomes a two-phase formation in a certain range of coverages. This interaction is taken into account phenomenologically in the Frumkin adsorption isotherm by the introduction of the attraction constant, at the critical value of which a first-order phase transition occurs.[11] Application of the LTJ method established that the cooperative rearrangement of the EDL takes place as a result of transitions of different orders.

In the present review the principles of the new method and the results of its application are consistently examined for the first time.

II. PULSE HEATING OF THE METALLIC ELECTRODE

The change in the temperature of the surface of a metal in contact with a solution under the influence of a light pulse absorbed by the metal is described by the relation (see, for example, Benderskii and co-workers):[3,7]

$$\Delta T(t) = \frac{L(1-R)}{\sqrt{\pi\varkappa c\rho}}\left(1+\sqrt{\frac{\varkappa_1 c_1\rho_1}{\varkappa c\rho}}\right)^{-1}\int_0^t \frac{f(t')}{\sqrt{t-t'}}\,dt' \quad , \tag{1}$$

where κ, c, ρ, κ_1, c_1, and ρ_1 are the thermal conductivities, heat capacities, and densities of the metal and solution respectively, L is the light intensity, R the coefficient of the reflection of light by the metal, and the normalised function $f(t)$ describes the form of the laser pulse. The maximum temperature jump generated by a pulse with a duration t_0 is

$$\Delta T_m = \frac{L(1-R)}{\sqrt{\pi\varkappa c\rho}}\left(1+\sqrt{\frac{\varkappa_1 c_1\rho_1}{\varkappa c\rho}}\right)^{-1}\sqrt{t_0} \quad . \tag{2}$$

The time variation of the surface temperature at $t \gg t_0$ is independent of the characteristics of the metal and is described by the relation

$$\Delta T(t) = \Delta T_m\sqrt{\frac{t_0}{t}} \quad . \tag{3}$$

Relations (1)−(3) are valid when the thickness of the electrode d and the size of the laser spot, i.e. the diameter of the heating zone r, satisfy the condition implying that the heat is removed solely along the normal to the interface and that there is no increase in the heated area:

$$d, r \gg 2\sqrt{\frac{\varkappa}{c\rho}t} \quad . \tag{4}$$

For a liquid mercury electrode placed in an aqueous solution ($\kappa = 7.9 \times 10^{-2}$ J cm^{-1} K^{-1} s^{-1}, $c = 0.14$ J g^{-1} K^{-1}, $\rho = 13.6$ g cm^{-3}, $\kappa_1 = 5.9 \times 10^{-3}$ J cm^{-1} K^{-1} s^{-1}, $c_1 = 4.2$ J g^{-1} K^{-1}, and $\rho_1 = 1.0$ g cm^{-3}) and illuminated with light at a wavelength 500−700 nm ($R \cong 0.70$ for normal incidence), the quantity $\Delta T_m/L = 2.2 \times 10^{-5}$ K kW^{-1} cm^2 when $t_0 = 4$ ns. This estimate shows that heating of the electrode by 1−2 K is effected by a light pulse with a peak power of 50−100 kW cm^{-2}. For the working electrodes with an area of approximately 10^{-3} cm^2 usually employed in measurements, this heating can be readily achieved with the aid of the usual nanosecond lasers having a peak power of 1−10 kW.

For observation times ranging from 10^{-8} to 10^{-6} s, the thicknesses of the heated layers of the metal and solution are $10^{-5}-10^{-4}$ cm and $10^{-6}-10^{-5}$ cm respectively, which means that the temperature jumps are localised outside the EDL in the bulk of the metal solution, i.e. the LTJ signal arises in the following galvanic cell:

metallic electrode	heated zone in the metal	heated zone in the solution	solution

and has three components:

$$\gamma_h = \gamma_{h1} + \gamma_{h2} + \gamma_{h3} \tag{5}$$

determined by the thermo-e.m.f. of the metal ($\mathscr{V}_{h3}$), the thermal diffusion potential of the solution ($\mathscr{V}_{h2}$), and the temperature coefficient of the decrease in the potential of the EDL $\mathscr{V}_{h1}$. The temperature jump induces a change in the potential of the EDL due to the temperature variation of its capacitance and composition. When the time constant of the electrochemical cell is large compared with the observation time, the outer source of polarisation does not have sufficient time to alter the initial charge of the electrode q, so that $\mathscr{V}_{h1}$ is recorded under coulombostatic conditions. The following relations are valid for low values of ΔT:

$$\mathscr{V}_{h1}=\left(\frac{\partial\varphi}{\partial T}\right)_q\Delta T,\ \mathscr{V}_{h2}=\alpha\Delta T,\ \mathscr{V}_{h3}=\alpha_s\Delta T \tag{6}$$

where $(\partial\phi/\partial T)_q$ is the temperature coefficient of the decrease in the potential in the EDL. When $q = 0$, this quantity is known for a series of electrochemical systems[12,13] and is of the order of magnitude of 10^{-3} VK^{-1}, which exceeds by two orders of magnitude the coefficients of the thermo-e.m.f. α of metals, i.e. $\mathscr{V}_{h1}\gg\mathscr{V}_{h2}$. The coefficient α_s is given by [14]

$$\alpha_s=\sum_i\frac{t_i}{z_i}S_i \tag{7}$$

where S_i is the transport entropy of ions of the ith kind having a charge z_i and a transport number t_i. The values of α_s for ions without anomalous mobility are of the order of 10^{-5} VBK^{-1}, so that the contribution of thermal diffusion to the LTJ signal can also be neglected. For solutions containing the anomalously mobile hydrogen and hydroxide ions, this contribution is significant and adds to $\mathscr{V}_h$ a component which is independent of the electrode potential.[7] With this exception, the LTJ signal is determined with adequate accuracy by the characteristics of the EDL and not the bulk phases:

$$\mathscr{V}_h\simeq\left(\frac{\partial\varphi}{\partial T}\right)_q\Delta T\ . \tag{8}$$

III. TEMPERATURE COEFFICIENTS OF THE POTENTIAL DROP IN THE ELECTRICAL DOUBLE LAYER

For a constant potential and phase composition, the equation of the electrocapillary curve is

$$-\mathrm{d}\gamma=\Gamma_s\mathrm{d}T+q\mathrm{d}E_\pm+\Gamma_\mp\mathrm{d}\mu\ , \tag{9}$$

where γ is the surface tension, $\Gamma_\pm$ the relative excess surface amounts of cations and anions respectively, $E_\pm$ the potential of the electrode, measured relative to the reference electrode, reversible with respect to the cations or anions, and Γ_S the excess surface entropy defined by the relation

$$\Gamma_S=S_{int}-m_M^\sigma S_M^0-m_W^\sigma\left(S_W^0-\frac{n_S}{n_W}S_S^0\right) \tag{10}$$

where S_{int} is the specific surface entropy, m_M^σ and m_W^σ are the numbers of moles of the metal and water per unit surface area, n_W and n_S the volume fractions of water and the salt, and S_M^0, S_W^0, and S_S^0 the standard entropies of the metal, water and the salt. Instead of Γ_S, we shall introduce the excess entropy of formation of the EDL, which is equal to the difference between the entropies of the components at the interface and in the bulk phases:

$$S^\sigma=S_{int}-m_M^\sigma S_M^0-m_W^\sigma S_W^0-m_+^\sigma S_+-m_-^\sigma S_-\ , \tag{11}$$

where S_+ and S_- are the entropies of the ions at the given activity of the salt. Bearing in mind that the electrode charage is equal to the difference between the excess surface amounts of the ions, we find from Eqns.(10) and (11)

$$q=\Gamma_--\Gamma_+ \tag{12}$$

$$\Gamma_s=S^\sigma+\Gamma_\pm S_s\mp qS_\mp \tag{13}$$

For a 1:1 electrolyte, the relation between the potential measured relative to the reference electrode and the potential drop in the EDL is described by the expression

$$F\mathrm{d}E_\pm=F\mathrm{d}\varphi\mp S_-\mathrm{d}T\pm\frac{1}{2}RT\mathrm{d}\ln a\ , \tag{14}$$

where F is the Faraday. In Eqn.(14), account was taken of the fact that

$$\mathrm{d}\mu=-S_s\mathrm{d}T+RT\mathrm{d}\ln a;\ S_s=S_s^0-R\ln a,\ \frac{\mathrm{d}\mu_\pm}{\mathrm{d}\ln a}=\frac{1}{2}RT,$$

where a is the activity of the salt. On substituting Eqns.(12)–(14) in Eqn.(9), we find

$$-\mathrm{d}\gamma=q\mathrm{d}\varphi+RT\left(\Gamma_\pm\pm\frac{q}{2F}\right)\mathrm{d}\ln a+S^\sigma\mathrm{d}T \tag{15}$$

Under coulombostatic conditions, used in the LTJ measurements, the thermodynamic potential is represented by the function

$$\xi=\gamma+q\varphi\ , \tag{16}$$

and, on going over to the latter, we obtain the main relation

$$-\mathrm{d}\xi=-\varphi\mathrm{d}q+RT\left(\Gamma_\pm\pm\frac{q}{2F}\right)\mathrm{d}\ln a+S^\sigma\mathrm{d}T. \tag{17}$$

The cross differentiation of Eqn.(17) leads to the relations

$$-\left(\frac{\partial\varphi}{\partial T}\right)_{a,q}=\left(\frac{\partial S^\sigma}{\partial q}\right)_{a,T}\ , \tag{18}$$

$$\left(\frac{\partial S^\sigma}{\partial\ln a}\right)_{q,T}=R\left(\Gamma_\pm\pm\frac{q}{2F}\right)+RT\left(\frac{\partial\Gamma_\pm}{\partial T}\right)_{a,q}\ . \tag{19}$$

The first of these relations constitutes the basis of the LTJ method and follows directly from the expression for the free energy of the charged interface:

$$\Delta G^\sigma=\Delta Q_0^\sigma+\int_0^q\varphi(q)\mathrm{d}q\ , \tag{20}$$

where ΔG_0^σ describes the non-electrical component of the free energy related, in particular, to the chemisorption and interaction of the adsorbed species with one another. Eqn.(19) relates the derivative of S^σ with respect to the activity of the salt to the temperature coefficient of the surface excess amounts. Under coulombostatic conditions, the first part of Eqn.(19) is the same for the anions and cations by virtue of relation (12). Differentiation of Eqn.(19) with respect to q yields the dependence of $V_h=(\mathscr{V}_h/\Delta T)=(\partial\varphi/\partial T)_{a,q}$ on the salt concentration:

$$\left(\frac{\partial V_h}{\partial\ln a}\right)_q=-R\left[\left(\frac{\partial\Gamma_\pm}{\partial q}\right)_{a,T}\pm\frac{1}{2F}\right]-RT\left(\frac{\partial^2\Gamma_\pm}{\partial q\,\partial T}\right)_a. \tag{21}$$

It follows from Eqn.(18) that, by measuring the dependence of V_h on q by the LTJ method, it is possible to find $S^\sigma(q)$ to within a constant, which is independent of q:

$$S^\sigma(q)=S^\sigma(0)+\int_0^q V_h(q)\mathrm{d}q\ . \tag{22}$$

Eqn.(21) relates the concentration variation of V_h to the surface excess amounts of the ions and their temperature coefficients.

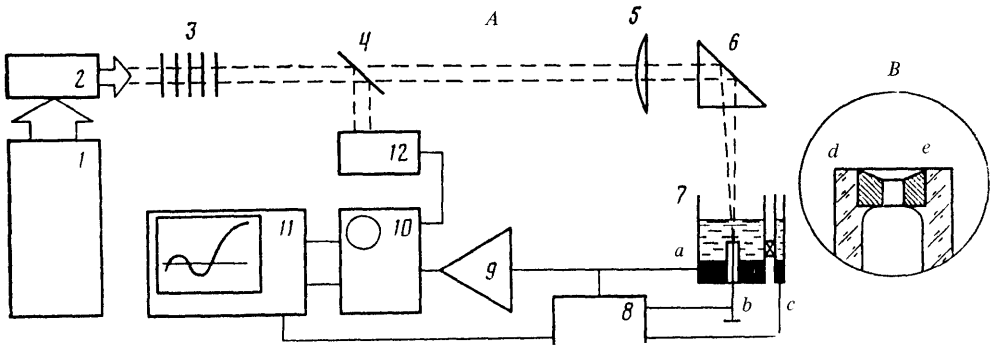


Figure 1. Circuit of the laser electrochemical relaxometer: 1) nitrogen laser used to pump the dye-based laser; 2) and 3) set of calibrated light attenuators; 4) semitransparent plate; 5) focussing lens; 6) rotatable prism; 7) electrochemical cell [*a*) measuring electrode; *b*) polarising electrode; *c*) reference electrode]; 8) polarisation and electrode potential scanning circuit; 9) amplifier of the LTJ signal; 10) stroboscopic oscillograph; 11) two-coordinate pen recorder; 12) circuit for the recording of laser pulses and the synchronisation of the strobe illumination (*A*); *B*) design of the working electrode in the electrochemical cell 7 [*d*) glass capillary; *e*) platinum ring].[7]

IV. METHODS OF MEASUREMENT

The LTJ method has been described in detail.[7] The circuit of the laser electrochemical relaxometer, designed for LTJ measurements, is illustrated in Fig.1. Heating is achieved by means of pulses from a laser based on rhodamine 6G (λ = 595 nm). At the selected light wavelength, the influence of photoemission can be neglected at electrode potentials more positive than −1.5 V.† The duration of the laser pulse is 4 ns for a peak power of 3 kW. The form of the pulse is recorded by a high-speed photocell. The laser light is focussed onto the cathode of the electrochemical cell. The LTJ signal is amplified by a broad band amplifier with a transmission band of approximately 200 mHz and is recorded by means of a stroboscopic oscillograph. When the frequency of the repetition of the laser pulses is 25 Hz, the stroboscopic conditions in the recording of the LTJ signal ensure its averaging over approximately 10^3 pulses, which makes it possible to achieve a sensitivity of the apparatus of 4×10^{-5} V, corresponding to minimum measurable values of V_h of 2×10^{-5} V K^{-1}. Further increase of sensitivity has been achieved[15] by employing a multichannel analyser in which the LTJ signal is divided by the amplitude of the laser pulse, which diminishes the error associated with the scatter of its values. Since the values of $(\partial\varphi/\partial T)_{q=0}$ for a series of solutions are known from independent electrochemical measurements,[10,11] the apparatus is calibrated directly in units of V_h and not γ_h, which eliminates the error associated with the determination of ΔT.

The working mercury electrode of the electrochemical cell (Fig.1) is made in the form of a smooth surface produced at the top of a glass capillary into which a thin platinum ring 0.35 mm in diameter has been sealed. As a result of the wetting of the ring with mercury, it is possible to avoid the appearance of capillary waves,[16] which interfere with the measurements, up to values of L = 1 MW cm^{-2}.

The $V_h(E)$ dependences are measured at a fixed instant. The delay of the instant of measurement relative to the maximum in the laser pulse is set at between 10 and 250 ns. The automatic scanning of the potential is performed after 30 − 100 s and the electrode surface is renewed after recording each $V_h(E)$ curve. The time variations of V_h are measured at constant electrode potentials. The relaxation time τ is determined by comparing the $V_h(t)$ kinetic curves with the curves calculated by Eqn.(1) for the measured form of the laser pulses. The relative values of τ for different E can be found to within 2 − 3 ns. The absolute values of τ contain a constant component which is determined by the transient characteristics of the cell and the amplifier. According to Benderskii and Velichko,[7] this component can be reduced to 5 − 10 ns. Konovalov and Raitsimring[15] succeeded in reducing its contribution to 1 − 2 ns.

In principle, the values τ may be found from the measured frequency dispersion of the differential capacitance. However, the scope of the high-frequency measurements is restricted by the time constant of the electrochemical cell, determined by the finite resistance of the volume of the electrolyte.[13,17] The maximum frequency of the measurements, attained at the present time, is 2 MHz and does not permit the observation of the relaxation of the EDL in the absence of the specific adsorption of organic substances.[17] The LTJ method is the only one which permits measurements of τ shorter than 10^{-6} S.

Eqn.(8) established a relation between V_h and the temperature coefficients of the differential capacitance of the EDL:

$$V_h = \left(\frac{\partial\varphi}{\partial T}\right)_{q=0} + \int_0^q \frac{\partial}{\partial T}\left(\frac{1}{C}\right) \mathrm{d}q \ . \qquad (23)$$

$$\frac{\partial V_h}{\partial q} = \frac{\partial}{\partial T}\left(\frac{1}{C}\right) \ . \qquad (24)$$

The validity of these relations in aqueous 0.5 M NaF solutions, for which the values of $\partial/\partial T(1/C)$ are known,[18,19] has been confirmed.[7] The $V_h(E)$ relations, measured by the LTJ method in aqueous 0.5 M NaF solution, agree with the relations calculated from the electrochemical data available for this solution,[18,19] which constitutes a test of the method. It must be emphasised that the accuracy of the determination of $V_h(E)$ from the temperature coefficients of the differential capacitance of the EDL is much lower than in the LTJ method. Despite the high accuracy of the measurement of C, reaching values to within 0.1 and 0.2% (see, for example, Charles et al.[20]),

† The potentials are read relative to the potential of the saturated calomel electrode.

the error in the measurements of $\partial C/\partial T$ is 5–10% owing to the smallness of the changes in C with temperature (0.01–0.10 F K^{-1}); integration with respect to E of the variable-sign function $\partial C/\partial T$, which enters into Eqn.(23), leads to errors in V_h up to 10–20%, increasing in the region of positive potentials under absorption conditions as a consequence of the increase in C. For this reason, there have been few calculations of the $S^\sigma(q)$ relations from electrochemical data.[20-23] Such measurements have been confined to the region of comparatively low positive charges ($q \leqslant 10$ μC cm^{-2}) and did not permit the discovery of a number of features of the EDL observed by the LTJ method.

V. THE LASER TEMPERATURE JUMP IN DILUTE ELECTROLYTE SOLUTIONS

According to the Gouy–Chapman theory, V_h is the sum of the temperature coefficients of the potential drop in the dense (φ^{M-2}) and diffuse (φ_2) parts of the EDL:

$$\left(\frac{\partial\varphi}{\partial T}\right)_q = \left(\frac{\partial\varphi^{M-2}}{\partial T}\right)_q + \left(\frac{\partial\varphi_2}{\partial T}\right)_q \qquad (25)$$

and the latter is given by

$$\left(\frac{\partial\varphi_2}{\partial T}\right)_q = \frac{\varphi_2}{T}\left(1 - \frac{kT}{e\varphi_2}\tanh\frac{e\varphi_2}{2kT}\right) . \qquad (26)$$

By measuring the dependence of V_h on q at different activities of the electrolyte and using Eqns.(25) and (26), two main postulates of the EDL theory have been tested:[7,24,25] the independence of the structure of the dense part of a, i.e. the constancy of $(\partial\varphi^{M-2}/\partial T)_q$ when a varies, and the validity of Eqn.(26), according to which the dependences of V_h on $(\partial\varphi_2/\partial T)_q$, calculated from Eqn.(26) for a different q should be represented by straight lines with identical slopes of unity. A similar method of testing the EDL theory has been used in the analysis of the differential capacitance curves.[2] The excess entropy of formation of the diffuse part of the EDL is

$$\Delta S_2 = -q\frac{\varphi_2}{T}\left(1 - \frac{3kT}{e\varphi_2}\tanh\frac{e\varphi_2}{4kT}\right) . \qquad (27)$$

If the theory is valid and ΔS^{M-2} is constant at different electrolyte activities, the relations between S^σ and ΔS_2 should be represented, as in the case of V_h, by straight lines with a slope of unity.

The $V_h(E)$ relations for the mercury electrode in aqueous NaF solutions with different electrolyte concentrations intersect at one point corresponding to the ZCP. As shown in Fig.2, the relations between V_h and $(\partial\varphi_2/\partial T)$ agree well with Eqns.(25) and (26) for $E \lesssim -0.1$ V. In the region of more positive potentials, the deviations exceed somewhat the insignificant adsorption of the fluoride ions. The excess entropy of formation of the EDL diminishes as the solution is diluted. The experimental relation between S^σ and ΔS_2 corresponds to the Eqn.(27).

Thus the results of the measurements agree well with the classical theory of the diffuse double layer in dilute electrolyte solutions (at concentrations below 0.1 M) in the absence of specific adsorption. Previously this theory was repeatedly confirmed by differential capacitance measurements (see, for example, Delahay[2]) and the LTJ method has made it possible to demonstrate that the thermal characteristics of the EDL are also described satisfactorily by it. It is noteworthy that the LTJ method not only yields an independent test of the theory of the concentration-dependent diffuse double layer but also makes it possible to find the values of φ_2 under conditions remote from the ZCP, where the influence the electrtolyte concentration on the CE curves is weakest and the accuracy of the determination of φ_2 by the differential capacitance method is reduced.

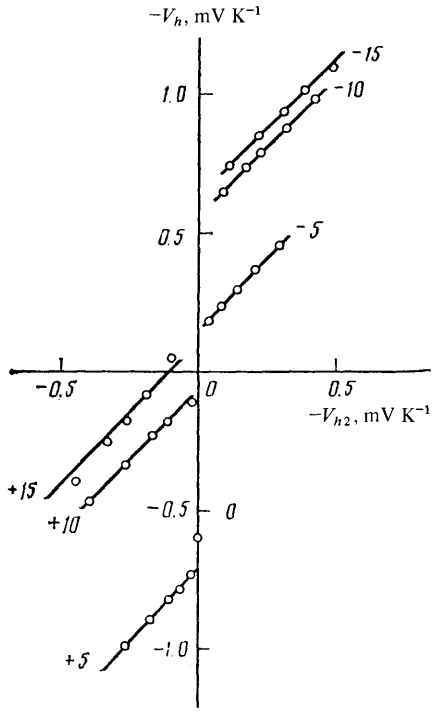


Figure 2. Dependence of V_h on $(\delta\Phi_2/\delta T)_q$ for different electrode charges (indicated in the figure in μC cm^{-2}); the continuous lines correspond to Eqns.(25) and (26).[25]

The kinetics of the LTJ signal in dilute solutions have been investigated in a study[6] where it has been shown that a slow increase in $V_h(t)$ takes place in the vicinity of the ZCP and that the characteristic time of the increase rises in inverse proportion to the electrolyte concentration. The theoretical description of the relaxation of the diffuse part of the EDL, based on the simultaneous solution of the continuity equations for the currents due to ions of both signs and the Poisson equation, shows that the spatial-time variation of the charge density is described by the same equation as the relaxation of the Debye atmosphere.[26] For a low initial change in the potential, its decrease takes place with a characteristic time given by

$$\tau_d = \varkappa^2 D,\ \varkappa^2 = \frac{8\pi e^2 a}{\varepsilon kT} , \qquad (28)$$

where $\varkappa^{-1}$ is the Debye length and D the coefficient of the dipolar diffusion of ions. The characteristic EDL relaxation times in the vicinity of the ZCP, measured by Benderskii et al.,[6] increase from 10 to 50 ns if the electrolyte concentration is reduced from 0.01 to 0.002 M, i.e. the $\tau_d(a)$ relation agrees with Eqn.(28).

As stated above, in the classical EDL theory it is assumed that the properties of its dense part in the absence of specific adsorption are independent of the electrolyte concentration. To test this principal hypothesis of the theory, measurements have been made[27] by

the LTJ method of the $V_h(E)$ relation in KF solutions at concentrations ranging from 1 to 12 M. A characteristic feature of this electrolyte[28] is the independence of the ZCP of the salt concentration and the insignificant increase in the differential capacitance for high negative charges ($q < -15$ μC cm^{-2}). Its more appreciable increase at $q \geqslant 0$ is attributed to the partial dehydration of the fluoride ions in such concentrated solutions, which dimishes the effective thickness of the EDL. According to Benderskii et al.,[27] the $V_h(E)$ and $S^\sigma(q)$ relations are also relatively insensitive to the KF concentration. Furthermore, the relaxation characteristics of the EDL hardly change, which means that the aqueous layer in the inner part of the EDL remains unaltered even at such high concentrations of the specifically non-adsorbable ions where the number of molecules in the bulk of the solution is no longer sufficient for the formation of the hydration shells, which are produced in dilute solutions.

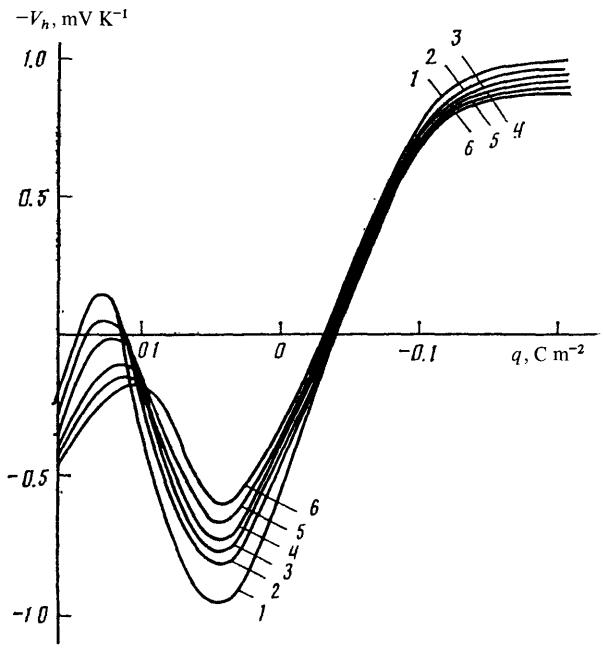


Figure 3. The $V_q(q)$ relations at different temperatures (°C): 1) 10; 2) 20; 3) 30; 4) 40; 5) 50; 6) 60; mercury electrode in aqueous 0.9 M NaF solution.[9]

At first sight, the agreement with experiment of the simple EDL theory over such a wide range of electrolyte concentrations is surprising bearing in mind that concentrated solutions are not described by the Debye–Hückel theory, which constitutes the basis of the simple EDL theory. The main reason for the observed agreement is apparently the independence of the structure of the dense part of the EDL of the electrolyte concentrations, by virtue of which a sharp dependence of the dielectric characteristics on the concentration and size of the ions, predicted by modern electrolyte models (see Carnic and Torrie's review[29]), is not manifested in the observed integral characteristics of the EDL.

VI. THE EXCESS ENTROPY AND HEAT CAPACITY OF THE DENSE PART OF THE ELECTRICAL DOUBLE LAYER

As can be seen from Figs.3 and 4, in the absence of specific adsorption, the $V_h^{M-2}(E)$ curves for the mercury electrode have three ZRP, implying that the dependence of the excess entropy of formation of the dense part of the EDL on the electrode charge is characterised by a minimum and two maxima in the vicinity of which there is a sharp increase in the relaxation time. With increase in temperature, the $S^\sigma(q)$ curves becomes gradually symmetrical relative to the $q = 0$ axis: the maximum and minimum in S^σ in the vicinity of $q > 0$ disappear above 40 °C, while the maximum at $q < 0$ shifts from -4.2 to -3.6 μC cm^{-2} in the range 0–65 °C.[8,9]

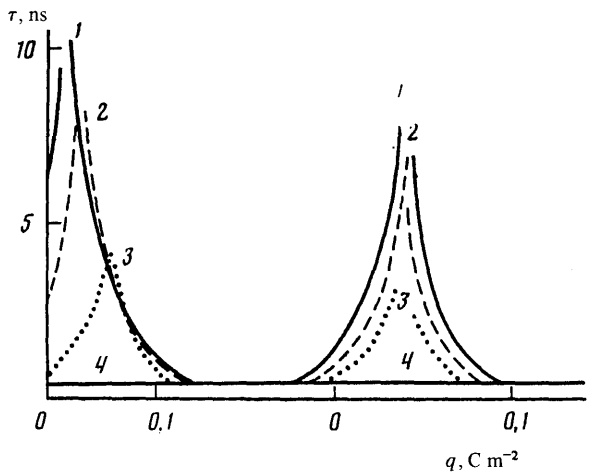


Figure 4. $\tau(q)$ relations at different temperatures °C: 1) 10; 2) 20; 3) 40; 4) 60; mercury electrode in aqueous 0.96 M NaF solution; accuracy of the measurement of τ to within 2 ns.[9]

The excess heat capacity of formation of the dense part of the EDL, given by

$$c^\sigma = T\left(\frac{\partial S^\sigma}{\partial T}\right)_{q,a} . \qquad (29)$$

has been found[9] from the temperature variation of $S^\sigma(q)$. The $S^\sigma(q)$ and $c^\sigma(q)$ relations at different temperatures are presented in Fig.5.

The properties of the dense part of the EDL are determined by the monolayer of the dipolar solvent molecules adsorbed on the metal.[1] By virtue of the interaction of the dipoles with the EDL field and with one another and also by virtue of specific adsorption forces, this two-dimensional layer undergoes orientational ordering. The orientation of the dipole depends on the field strength in the inner part of the EDL, i.e. on the charge of the electrode, which leads to a non-linear $q(E)$ relation. The decrease in the potential within the dense part of the EDL can be represented in the form

$$\varphi = \frac{\delta}{\varepsilon} q + \frac{Np}{\varepsilon} f(q) , \qquad (30)$$

where δ is the effective thickness of the dense part of the EDL, ε is its dielectric constant in the absence of orientational polarisation, determined by the molecular polarisability of the solvent molecules, and N and p are the surface density and the dipole moment of the

solvent molecules. The function $f(q)$ characterises the degree of orientation of the dipoles. In strong electric fields (for $q \to \pm\infty$), the dipoles are fully oriented and $f = \pm 1$, so that, for constant δ/ε and Np/ε, f becomes a linear function of q. According to Trasatti,[30,31] the $\varphi(q)$ curves for aqueous electrolyte solutions are not only linear but also have the same slope for different *sp* metals in the region of high negative potential ($q \leqslant -10$ μC cm^{-2}), which indicates the universality of Eqn.(30).

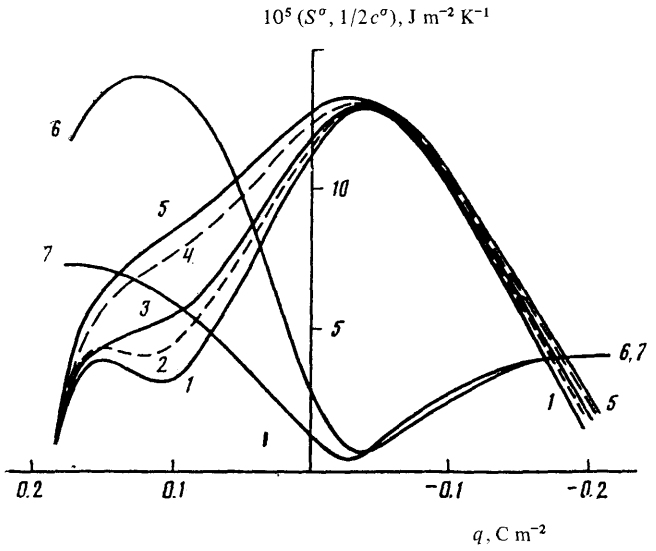


Figure 5. $S^\sigma(q)$ (curves *1*–*5*) and $c^\sigma(q)$ (curves *6* and *7*) relations at different temperatures (°C): 1) 10; 2) 20; 3) 40; 4) 60; 5) 70; 6) 15; 7) 65; mercury electrode in aqueous 0.96 M NaF solution.[8]

In the initial model of the two-dimensional,[32] two possible dipole orientations were considered. In this case f is determined by the numbers of dipoles oriented along the electric field and in opposition to it and in the case of isolated dipoles is described by the relation

$$f = \frac{N_+ - N_-}{N} = \tanh u, \quad u = \frac{p}{\varepsilon kT}(q - q^*) \ . \tag{31}$$

For $q = q^*$, both orientations are equally probable and $f = 0$. The characteristic charge q^* is non-zero as a consequence of the difference between the free energies of adsorption for the two orientations. The potential at which $q = q^*$ is identical with the ZRP, because the orientational entropy is a maximum for $N_+ = N_-$. The $\tau(q)$ relation is described by the expression

$$\tau = \frac{\tau_0}{\cosh u} \tag{32}$$

and also has a maximum equal to τ_0 at $q = q^*$. Thus in the two states model the ZRP is universal for all metals for which Eqn.(30) holds and corresponds to the absence of a dipole potential jump, i.e. to $f = 0$.

Since the two states model does not lead to a quantitative description of the differential capacitance curve (*CE* curves) at different temperatures, models have been developed with a larger number of states (see, for example, Refs.33–38) taking into account the possibility of the formation of dipolar associated species in the two-dimensional layer.‡ In the presence of n states of the $2d$ layer, the number of ZRP is at least $n - 1$ regardless of the characteristics of these states.[39] Each of them corresponds to a local entropy maximum determined by the equality of the probabilities of two definite states. For example, in the three states model[37] (two opposite orientations of the dipoles and their aggregates which have no moment), the $S^\sigma(q)$ relation should have two maxima corresponding to the conversion of the dipoles into aggregates. Curves *1* and *2* shown in Fig.5 can be regarded as experimental proof of the existence of at least three states of the water dipoles in the two-dimensional layer. However, the $\tau(q)$ relations do not agree with the hypothesis of the existence in the two-dimensional layer of isolated water molecules and their low-molecular-weight associated species, because in this case, as in the two level model, the decrease in $\tau(q)$, like that in $S^\sigma(q)$, is determined by u and may occur over a wide range of q values. The pronounced $\tau(q)$ relation is clearly not described by Eqn.(32) and indicates a cooperative character of the rearrangement of the $2d$ layer at the ZRP, which is not described by the models put forward in the literature.[32–39] It has been suggested[8,9] that, in the region located between the ZRP ($q_1 < q < q_2$, q_1 and q_2 correspond to the ZRP), there exists below 40 °C an ordered state of the water molecules of the type of two-dimensional ice, which is decomposed by the electric field at the ZRP as a result of the reorientation of the dipoles. The disruption of the antiferromagnetic ordering in strong magnetic fields is an analogue of this process.[40] The free energy of an ordered state of the antiferroelectric type increases with increase in $|q - q_0|$ (q_0 corresponds to the minimum in S^σ) and a structural phase transition to a paraelectric state, whose energy diminishes with increase in $|q - q_{1,2}|$, occurs at the points q_1 and q_2. Above 60 °C, the paraelectric state exists at all values of q, which is indicated by the disappearance of the ZRP, corresponding to q_1 and q_0, and of the $\tau(q)$ peaks. The $S^\sigma(q)$ and $c^\sigma(q)$ relations in this state agree with relations calculated in terms of the molecular field approximation[41] for reasonable values of the parameters: $p = 1.3$ D and $N = 2 \times 10^{15}$ cm^{-2}.[9] The fluctuation theory of phase transitions has been used for the description of the $2d$ layer at lower temperatures.[8,9] The singular part of the free energy in the critical region Φ_S is a function of the parameter $A(T - T_c)$,[43] in which A and the critical temperature T_c depend on $(q - q_0)^2$, provided that the order parameter $l \propto (q - q_0)^2$. The equation for the critical values, $A(T - T_c) = 0$, has two roots:

$$q_{1,2} = q_0 \pm \Delta(T) \ . \tag{33}$$

The $\Phi_S(q)$, $l(q)$, and $\tau(q)$ relations are determined by the values of the universal critical indices:

$$\Phi_S \propto U^{2-\alpha}, \ l \propto U^{\beta}, \ \tau^{-1} \propto \frac{\partial^2 \Phi_S}{\partial l^2} \propto U^{2-\alpha-2\beta}, \qquad U = B(T)\,|\,(q - q_0)^2 - \Delta^2(T)\,| \ , \tag{34}$$

where $B(T)$ is a non-singular function of temperature. It follows from Eqn.(34) that the increase in the relaxation time should occur at the points q_1 and q_2, where the order parameter l becomes zero,

‡ Despite the difference between the numbers of states and the values of the parameters (the adsorption energies, the dipole moments, N and ε), all these models make it possible to describe satisfactorily the *CE* curve at different temperatures, which, rather than indicating the reliability of these models, is more likely to be evidence for the insensitivity of the experimental data to their choice, associated with the large number (5–7) of parameters, which are in essence adjustable.

and $S^{\sigma}(q)$ is a maximum. In agreement with the hypothesis of the universality of the critical indices, the values of $\gamma = 2 - \alpha - \beta$ are identical at the points q_1 and q_2 and amount to approximately 0.7.

It is noteworthy that at the critical points the maxima in the second derivatives of Φ_S with respect to q and T (the differential capacitance, V_h, and c^{σ}), which are the usual signs of second-order phase transitions, are not observed. The absence of singularities on the curves indicated can apparently be accounted for by the fact that they are determined by the low critical index α, which may be close to zero for two-dimensional systems.[42] On the other hand, the $\tau(q)$ singularities are determined by the larger critical index γ and for this reason are easier to observe experimentally. Furthermore, the ordered state of the non-commensurate lattice on the surface of the liquid metal is most likely to be appreciably converted into an amorphous form, which widens the region of the transition. This is indicated, in particular, by the higher heat capacity of the antiferroelectric state compared with the paraelectric state (Fig.5).

The phase transitions in the two-dimensional layers have been the subject of vigorous research (see Vilches' review[44]) and in this connection one may point to a series of systems whose behaviour is close to that of the new EDL model proposed by Benderskii and co-workers.[8,9] For example, the transition from the planar to the perpendicular oreintation of nitrogen[45] and ethane[46] molecules as well as the dimerisation of nitric oxide[47] have the character of phase transitions. In most cases the lattice parameteers of two-dimensional crystals close to the three-dimensional parameters are incommensurate with the lattice of the support. On the basis of these data, one can hardly be surprised that water molecules on the surface of metals are capable of forming an ordered structure.

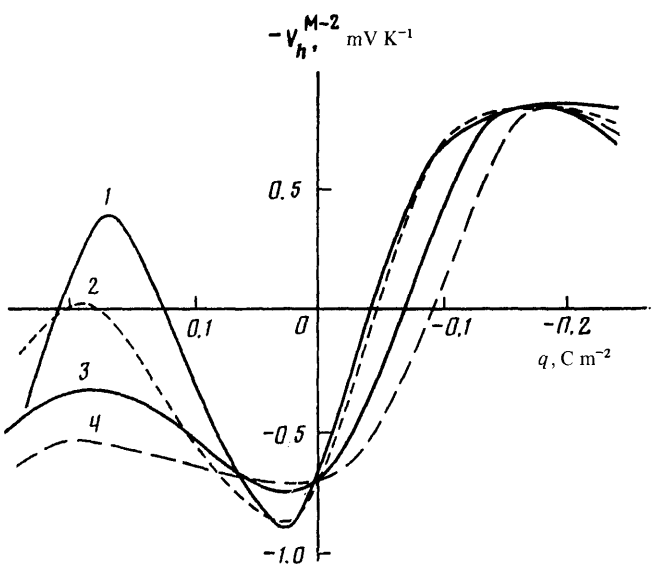


Figure 6. $V_h^{M-2}(q)$ relations at the interface between the mercury electrode and 1 M aqueous solutions of different salts: 1) KF; 2) KCl; 3) KBr; 4) KI.[50]

The values of τ in the vicinity of the ZRP, measured[7] for different *sp* metals, amount to $10^{-7}-10^{-8}$ s, while in the ordering region they do not exceed 3×10^{-8} s. Comparison of these values with the dipolar relaxation times in liquid water ($\sim 10^{-11}$ s) and in ice crystals ($\sim 10^{-5}$ s at 0 °C) makes it possible to infer the mobility of water molecules at the interface. The rotation of dipoles in ice crystals is due to the translational movement of Bjeruum defects.[48] In the cavities within vitreous ice, the rotational relaxation time at -10 °C is approximately 10^{-10} s.[49] Presumably at $q \leqslant 0$, where water molecules form M–O bonds with the surface, the rotation of the dipoles does not entail the rupture of these bonds and takes place similarly to relaxation in liquid water and not in the crystal.

In conclusion of this Section, we shall deal with the question of the correspondence of the ZRP and the potential at which there is no dipole jump. As stated above, these potentials agree only in the two state model. For $n > 2$, in the general case none of the ZRP correspond to $f = 0$ and the identification of the ZRP for $q < 0$ with the potential at which $f = 0$, postulated in a number of investigations,[22,30,31,35] requires a more careful study, like the determination of the dipole jumps at the ZCP based on it. The latter jumps are regarded as a measure of the hydrophilicity of metals.[1,30] The difference between ZCP and ZRP (for $q < 0$) diminishes with increase in hydrophilicity in the sequence Hg, Pb, Bi, Cd, Ga. The values of $-q_2$, corresponding to the ZRP, decrease in the same sequence as a result of the increase in the slope of the qE curves in the region of low values of q.[7]

VII. ADSORPTION OF ANIONS

The $V_h(E)$ curves for aqueous KCl, KBr, and KI solutions (Fig.6) differ in the region of the adsorption of halide ions.[50] In analysing these curves, it is necessary to take into account the contribution to $(\partial\varphi_2/\partial T)$ by the temperature coefficients of the excess adsorbed surface anions:

$$\left(\frac{\partial q_1}{\partial T}\right)_q = q_1 \frac{\Delta G_a}{RT}(1 + B_2\Gamma_i)^{-1}, \qquad (35)$$

where $q_1 = F\Gamma_i$, Γ_i is the surface excess, ΔG_a the free energy of adsorption, and B_2 the second virial coefficient, which is known from electrochemical data.[51]

The $S^{\sigma}(q)$ relations, found taking into account the correction defined by Eqn.(35), are illustrated in Fig.7. The adsorption of anions leads not only to a decrease in S^{σ} but also to the disappearance of the ZRP in the region $q > 0$, which is accompanied by the simultaneous disappearance of the relaxation time peak. The $\tau(q)$ peak is retained in 1 M KCl solution at $q < 0$ but its width becomes smaller than in the fluoride solution. In the region of the adsorption of BR^- and I^-, an increase in τ to 5–6 and 8–10 ns respectively is observed. The disappearance of the $S^{\sigma}(q)$ minimum shows that the specific adsorption of ions disrupts the ordered state of the two-dimensional layer, in particular as a consequence of the change in the orientation of the dipoles participating in the formation of the hydration shells of the adsorbed ions.§ Within the framework of the theory,[42] the introduction of impurities into the 2*d* layer decreases the critical transition temperature, which is taken into account in Eqn.(33) by the function ΔT, which depends on the degree of coverage θ:[54]

$$\frac{\Delta(T,\theta)}{\Delta(T,0)} = \begin{cases} 1-\theta, & \theta \ll \theta_c, \\ |\theta - \theta_c|^{f_c}, & \theta \propto \theta_c, \end{cases} \qquad (36)$$

§ It has been suggested[52,53] that the hydration shells of ions do not undergo major distortion on adsorption. Quantum-chemical calculation[53] has shown that the disposition of the ion and free water molecules in a single plane corresponds to the minimum energy of the hydrated Cl^- anion.

where θ_c is the permeation threshold at which the transition disappears and t_c is the critical index of the breakdown of the transition. In this model the disordering of the two-dimensional layer takes place, judging from the disappearance of its cooperative rearrangement at the ZRP already at comparatively low degrees of coverage ($-q_1 = 3-5$ μC cm^{-2}) corresponding to average distances of 2–3 nm between the adsorbed ions. The EDL relaxation time in the adsorption region is apparently determined by the movement of the adsorbed ion and its higher value compared with the Debye relaxation time characterising the relaxation of ions in the diffuse part of the EDL (see above) reflects the decrease in the mobility of ions and their hydration shells on adsorption.

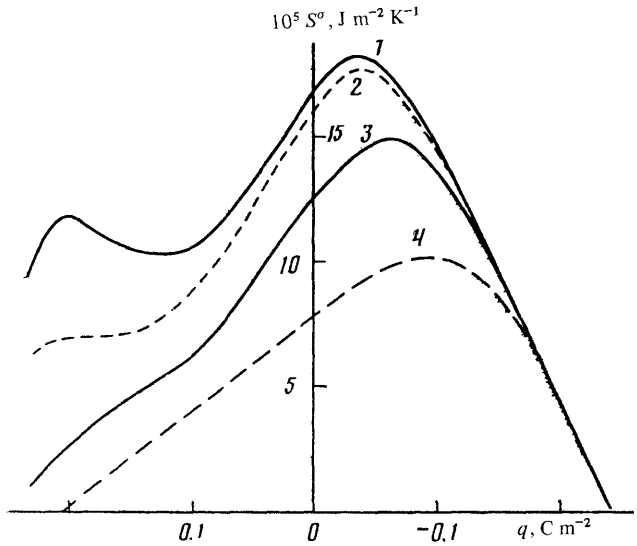


Figure 7. $S^\sigma(q)$ relations at the interface between the mercury electrode and 1 M aqueous solutions of different salts: 1) KF; 2) KCl; 3) KBr; 4) KI.[50]

The values of B_2 can be found by comparing the $S^\sigma(q)$ curves in solutions of specific adsorbable ions and in the solution where there is no adsorption. The values of B_2 have been obtained[50] for Br^- and I^- (2.2×10^{-14} and 3.3×10^{-14} cm^2 respectively), which agree with other data,[20,55] and the relation between B_2 and q for Cl^-, noted by Charles et al.,[20] has been confirmed. Because of the repulsion of the adsorbed ions, their distribution on the surface with increasing Γ_i ceases to be random, which entails a decrease in S^σ. The increase in the electric field strength of the EDL, i.e. in q, causes disordering in the distribution of the adsorbed ions in the two-dimensional layer, i.e. a decrease in B_2.

The negative Gibbs adsorption of chloride ions at the interface between the mercury electrode and concentrated LiCl solutions, in which the activity of the salt changes almost by three orders of magnitude when its concentration c_S is raised from 1 to 12 M, ensuring a broad region in which the thermodynamic relations (19) and (21) can be tested, has been investigated[56] by the LTJ method. With increasing c_S, the $V_h(E)$ curves shift to the region of more negative potentials (Fig.8), the ZRP being located in the region more negative by 0.15–0.30 B than the ZCP, the difference between these potentials increasing, i.e. the maximum entropy occurs for more negative charges.

The shift of the ZRP is accompanied by a shift of the EDL relaxation region, the width of the $\tau(E)$ peak decreasing and the values of τ increasing. The $(\partial S^\sigma/\partial \ln c)_{q,T}$ for a concentrated LiCl solution do not agree with Grahame's theory not only in magnitude but also in sign. The temperature coefficients of the surface excess amounts found from Eqn.(19) for $q < -5$ μC cm^{-2} are $(\partial\Gamma_\pm/\partial T)_q > 0$ [according to Grahame's theory $(\partial\Gamma_\pm/\partial T)_q < 0$] and their absolute values are more than an order of magnitude greater than expected. Negative values of the theoretical coefficients are associated with the fact that an increase in temperature tends to equalise the ion concentrations in the solution and in the double layer. The observed positive values of $(\partial\Gamma_\pm/\partial T)_q$ imply that the excess surface amounts of ions of both signs are negative. Thus the sign of $(\partial\Gamma_\pm/\partial T)_q$ is a direct consequence of the negative adsorption of the salt for $q < 0$ noted in the literature.[28,57] In Grahame's theory the presence of non-adsorbable ions at the interface and in the bulk of the solution for $q = 0$ is assumed to be equally probable. Evidently this approximation breaks down if the hydration conditions in the bulk phase and at the interface are different. Such difference arises in concentrated electrolyte solutions where the number of water molecules is insufficient for the construction of the hydration shells of the ions.

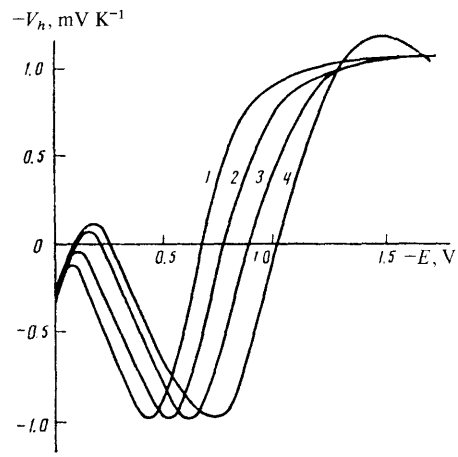


Figure 8. $V_h(E)$ relations at the mercury–concentrated aqueous LiCl solutions interface; LiCl concentration (M): 1) 1; 2) 4; 3) 8; 4) 13.7.[56]

In contrast to Grahame's theory, there is a broad range of values of q where the increase in c_S diminishes S^σ as a consequence of the ordering of the ionic component [of the EDL?], possibly on formation of a layered structure.[58] The retention of the form of the $V_h(q)$ curves and the EDL relaxation in the region of the ZRP for high values of c_S implies that water molecules remain in the inner part of the EDL even in very concentrated solutions which is also due to the negative adsorption of the salt.

If the water layer were located between the outer and inner Helmholtz planes, the shift of the ZRP should have corresponded to the constancy of $q + q_1$ and the charge at the ZRP should have increased with increase in $-q_1$, whereas in fact q diminishes. This means that the layer of water molecules is located between the metal and the inner Helmholtz plane (the plane corresponding to the maximum approach by the adsorbed ions). This hypothesis agrees with the data indicated above demonstrating a comparatively small deformation of the hydration shells of ions on adsorption.

VIII. ADSORPTION OF ORGANIC SUBSTANCES

The principal difference in the LTJ in the case of the adsorption of organic surfactants (OS) consists in the constancy of their surface excess Γ under the conditions of the pulse heating of the electrode, which is responsible for the short duration of the heat pulse compared with the time of attainment of the adsorption-desorption equilibrium and follows directly from the frequency dependence of the initial capacitance $C_1 = (\partial\Gamma/\partial E)(\partial\Gamma/\partial q)^{-1}_{T,c}$. This capacitance is observed at frequencies below 10^4 Hz,[59] while the times of the LTJ measurements do not exceed 10^{-6} s. For this reason, LTJ refers to non-equilibrium conditions relative to the bulk of the solution. On the other hand, in the heated layer near the electrode, there is sufficient time for diffusion to establish equilibrium between the surface excess and the OS concentration, i.e. the LTJ is measured under conditions described by the thermodynamic potential corresponding to the q, T, and Γ variables. For this potential, we have

$$V_h = \left(\frac{\partial\varphi}{\partial T}\right)_{q,\Gamma} = -\left(\frac{\partial S^\sigma}{\partial q}\right)_{T,\Gamma} . \quad (37)$$

In Eqn.(7), the component of V_h due to the thermal diffusion of the OS is neglected. In order to determine S^σ, it is necessary to convert the values of V_h into the derivative $(\partial S^\sigma/\partial q)_{T,c}$ measured at a constant OS volume concentration and not at a constant Γ. This change in the variables q, T, and μ leads to the relation

$$\left(\frac{\partial\varphi}{\partial T}\right)_{q,\Gamma} = \left(\frac{\partial\varphi}{\partial T}\right)_{q,c} + \left(\frac{\partial\varphi}{\partial \ln c}\right)_{q,T}\left(\frac{\partial \ln c}{\partial T}\right)_{q,\Gamma} , \quad (38)$$

which has been obtained[60] by the standard method involving the transformation of the variables of the thermodynamic functions[43] (p.83). On the assumption that the adsorption isotherm is congruent relative to the electric variable,[59] it can be expressed in the form

$$c\cdot\exp(-G_a/RT) = f(\Gamma) , \quad (39)$$

where ΔG_a is the free energy of adsorption, which depends on q but is independent of Γ. It follows from Eqns.(38) and (39) that

$$\left(\frac{\partial S^\sigma}{\partial q}\right)_{T,c} = -V_h + \frac{\Delta G_a}{T}\left(\frac{\partial\Gamma}{\partial q}\right)_{T,c} . \quad (40)$$

The surface pressure[2]

$$\Pi = RT\Gamma_m f(\Gamma) , \quad (41)$$

where Γ_m is the maximum coverage, corresponds to the isotherm (39). According to Everett,[61] we have

$$\left(\frac{\partial\Pi}{\partial T}\right)_\Gamma = -\Gamma_m\theta^2\left(\frac{\partial S^\sigma}{\partial\theta}\right)_{T,c} , \quad (42)$$

where $\theta = \Gamma/\Gamma_m$ is the degree of coverage. A relation between ΔG_a and the molar entropy of adsorption S_a follows from Eqns.(39) and (42):

$$S_a = \left(\frac{\partial S^\sigma}{\partial\Gamma}\right)_{T,c} = S_a^0 + \frac{\Delta G_a}{T} - R\ln c , \quad (43)$$

where S_a^0 is the part of the molar entropy of adsorption determined by the change in the internal degrees of freedom of the adsorbate. If structural changes in the adsorbate molecules, caused by their interaction, take place in the course of surface coverage, S_a^0 is a function of Γ. On substituting Eqn.(43) in Eqn.(40) and integrating with respect to q taking into account the fact that desorption takes place at high negative electrode potentials ($\Gamma = 0$ at $q \to -\infty$), we find

$$S^\sigma = S_1^\sigma + \Delta + S_\infty - R\Gamma\ln c , \quad (44)$$

where

$$S_1^\sigma = \int_0^\Gamma S_a^0\,d\Gamma, \quad \Delta = \int_{-\infty}^{q}\frac{\Delta G_a}{T}\left(\frac{\partial\Gamma}{\partial q}\right)_{T,c} dq . \quad (45)$$

S_∞ is the integration constant. Integration of Eqn.(40) under the same conditions yields

$$S^\sigma = S_h + \Delta + S_\infty , \quad (46)$$

where

$$S_h = -\int_{-\infty}^{q} V_h(q)\,dq . \quad (47)$$

Eqns.(44) and (46) establish a relation between S_h (the integral of V_h) and S^σ and its structural components S_1^σ:

$$S_h = S_1^\sigma - R\Gamma\ln c . \quad (48)$$

It follows from Eqn.(48) that the $S_h(q)$ relation describes the change in the EDL structure and is independent of the configurational component S^σ, which is given by $S_2^\sigma = \Delta - R\Gamma\ln c$. Since S_2^σ usually exceeds S_1^σ severalfold,[60] the $S_h(q)$ curves, i.e. the LTJ data, contain more information permitting the discovery of the structural changes in the EDL than the $S^\sigma(q)$ curves. The logarithmic dependence of S_h on the OS concentration is due to the definition of S^σ as the difference between the entropies of the components on the surface and in the bulk phases in the standard state, the transition to which corresponds to a change in $S = S^0 - R\ln c$. The above thermodynamic analysis is valid when the function $S^0(q)$ is continuous, which can be tested experimentally. If there are no jumps in S^σ in the region of adsorbability, the relation

$$\int_{-\infty}^{+\infty}[V_h(q, 0) - V_h(q, \Gamma)]\,dq = 0, \quad (49)$$

which follows from the condition that the values of S^σ are identical regardless of adsorbability of all OS concentrations, is valid.

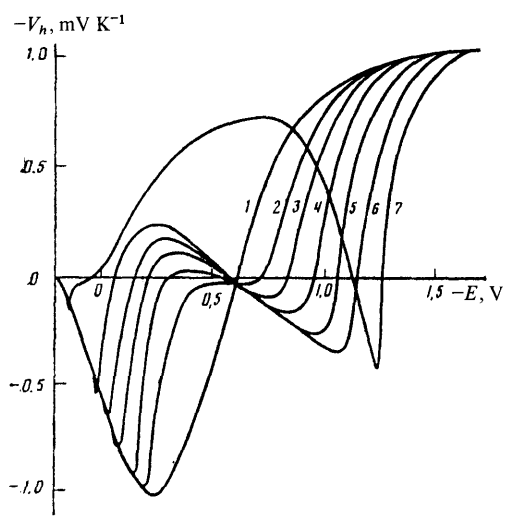


Figure 9. $V_h(E)$ relations at the interface between the mercury electrode and 1 N aqueous Na_2SO_4 solution with added n-pentyl alcohol at concentrations of 0, 5×10^{-3}, 1×10^{-2}, 1.5×10^{-2}, 3×10^{-2}, 5×10^{-2}, and 0.15 M (curves *1*–*7* respectively).[62]

The adsorption of aliphatic n-alcohols ranging from C_3 to C_6 on the mercury electrode has been investigated by the LTJ method.[60,62] Typical $V_h(E)$ relations are presented in Fig.9. With increase in the OS concentration, the deviations from the background V_h^0 curve

increase. For $\Gamma \cong \Gamma_m$, a second $V_h(E)$ section, with a constant positive slope corresponding to a quadratic $\Delta G_a(q)$ relation, appears. In the region of adsorbability, there are three ZRP.

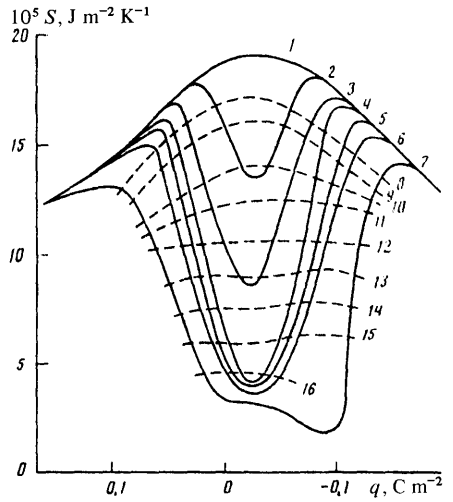


Figure 10. $S_h(q)$ relations in the adsorption of n-pentyl alcohol on the mercury electrode from aqueous 1 N Na_2SO_4 solution with the same OS concentrations as in Fig.9; the dashed curves *8—16* represent the $S^{\sigma}_{\Gamma}(q)$ relations for constant degrees of coverage ranging from 0.1 to 0.9 in 0.1 steps respectively.[60]

The extreme two of these potentials coincide with the potentials of the maxima on the $C(E)$ differential capacitance curves and correspond to degrees of coverage $\theta_c \cong 0.5$. The $V_h(E)$ curves for different c intersect at approximately one point corresponding to the maximum adsorption potential. A typical $S_h(q)$ relation is illustrated in Fig.10 and demonstratres the presence of two maxima and a minimum in the structural entropy of the EDL. The validity of Eqn.(48) has been verified.[60] The values of Γ_m found from the linear sections of the $S_h(\ln c)$ curves agree with the results of electrochemical measurements.[59] Fig.10 also presents the $S^{\sigma}_h(q)$ relations for constant Γ, calculated from the $S_h(q, c)$ curves by Eqns.(45) and (46) using the parameters of the adsorption isotherms taken from Damaskin et al.[59] The change in the form of the curves with increasing Γ shows that, for $\theta \gtrsim 0.4$, the adsorption of aliphatic alcohols cannot be regarded as the substitution of isolated water molecules by isolated OS molecules. The cooperative character of the rearrangement of the EDL is manifested by the sharp increase in relaxation time near the ZRP corresponding to the S_h maxima.¶ Theoretical analysis of the $V_h(E)$, $C(E)$, and $\tau(E)$ relations for the adsorption of OS has been carried out[63] on the basis of the ideas concerning the two-dimensional second-order phase transitions examined in Section V of this review. According to the present authors,[60,62] Eqn.(49) holds only at low concentrations of n-pentyl ($< 5 \times 10^{-2}$ M) and n-hexyl ($< 3 \times 10^{-2}$ M) alcohols. For higher values of c, a sharp decrease in V_h (down to $V_h < 0$) is observed and, after the break at the minimum, there is just as sharp an increase (to $V_h > 0$). The appearance of V_h peaks (Fig.9), corresponding to jumps in S_h (Fig.10), indicates the occurrence of first-order phase transitions.

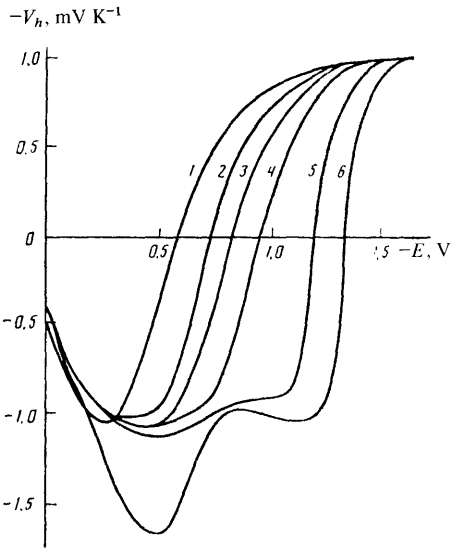


Figure 11. $V_h(E)$ relations for the adsorption of phenol on the mercury electrode from aqueous 0.5 M Na_2SO_4 solution; the phenol concentrations are 0, 4×10^{-3}, 2×10^{-2}, 4×10^{-2}, 0.1 and 0.4 M for curves *1—6* respectively.[64]

The LTJ method has been used[64] to investigate the adsorption of phenol and 1,3,5-trihydroxybenzene (THB). The choice of phenol was dictated by the fact that, according to Damaskin et al.[65] and Sarangapani and Venkatesan,[66] its adsorption, like that of the majority of aromatic OS, is possible in two orientations—planar and perpendicular, the second of which occurs at fairly high concentrations ($> 4 \times 10^{-5}$ M) in the vicinity of the ZCP, while the first obtains at high positive potentials.[67] Apart from the adsorption-desorption maxima, jumps in differential capacitance have been observed[66,68] in the adsorption of THB on mercury and were attributed to the formation of two-dimensional crystals of the THB dihydrate. The $V_h(E)$ curves for the above compounds are presented in Figs.11 and 12. The potentials for the $C(E)$ maxima coincide with the ZRP at different OS concentrations and are also characterised by EDL relaxation time peaks (Fig.13). In contrast to the systems examined previously (Fig.4), the $\tau(E)$ peaks are highly asymmetric. In the region of abrupt changes in capacitance in the course of the adsorption of THB, V_h peaks arise. The values of τ in the range of E between the ZRP and the V_h peak is much greater than in the supporting electrolyte and amounts to approximately 30 ns. In the vicinity of the V_h peak, i.e. in a first-order phase transition, there is

¶ The S^{σ}_{Γ} relations were known previously only for low degrees of coverage ($\theta < 0.4$) of the mercury electrode by thiourea.[23] It has been concluded[23] that S^{σ}_{Γ} is an additive function of the degree of coverage, consisting of two contributions, associated with the adsorbed water and OS molecules. LTJ data have shown that this conclusion cannot be extended to the range of higher coverages.

a sharp decrease in τ down to values less than 10 ns. It has been suggested[64] that the order of the phase transitions in the EDL can be determined from the following features of the $C(E)$, $V_h(E)$, and $\tau(E)$ curves (see Table). The simultaneous appearance of $C(E)$ peaks and $V_h(E)$ zero values at the second-order phase transition points follows directly from the form of the singular component of the thermodynamic potential (34) when Δ is independent of T. The constancy of the degree of coverage at which the transition takes place ($\theta_c \cong 0.5$) indicates its similarity to transitions of the order–disorder type; when $\theta < \theta_c$, random coverage of the nodes (adsorption sites) takes place and, when $\theta \cong \theta_c$, a state with a short-range order in their distribution arises. Such transitions in planar lattices have been investigated in fair detail.[44–47,69,70] The critical values of θ_c, corresponding to the formation of "an infinite cluster" of occupied nodes (the permeation threshold), depends on the lattice geometry, the configuration of the molecules, and their orientation in adsorption.[71,72]

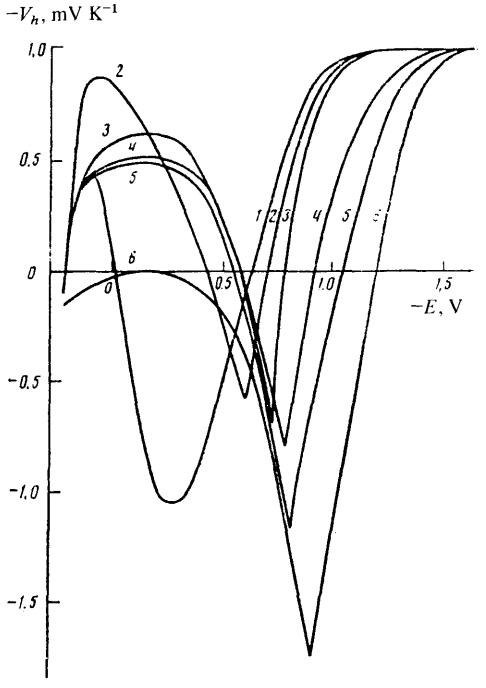


Figure 12. $V_h(E)$ relations for the adsorption of 1,3,5-trihydroxybenzene on the mercury electrode from aqueous 0.5 M $LiClO_4$ solution with OS concentrations of 0, 4×10^{-5}, 10^{-3}, 5×10^{-3}, 2×10^{-2}, and 0.1 M for curves *1*–*6* respectively.[64]

Although some of the features enumerated in the Table can be poorly expressed (for example, in the adsorption of aliphatic alcohols jumps in τ are not observed in first-order transitions, while in the adsorption of phenol one observes minima at low values of c instead of negative v_h peaks), nevertheless the combination of LTJ data and electrochemical measurements makes it possible to establish the occurrence and order of the phase transitions in the EDL when the potential is varied.

A characteristic feature of mixtures of water and aliphatic compounds with a terminal polar group (amphiphiles) is the formation of liquid crystal phases due to the fact that the equilibrium packing of the amphiphile molecules should ensure the shielding of the hydrophobic hydrocarbon chain from water. According to the cT diagram for amphiphile–water mixtures,[70] an increase in the amphiphile concentration entails a transition from a solution of isolated molecules to a micellar phase. On further increase in c, the micellar phase is converted into liquid crystal mesophases—hexagonal and lamellar, which are then converted into an amphiphile crystal. The micellar phase–mesophase transitions and the transitions between the mesophases can be both of the first and second order, while the mesophase–crystal transition is usually a first order transition of the type of fusion. Presumably structures with different disposition of the adsorption sites and different packing of the hydrocarbon chains are formed at the interface between the metal and the aqueous solution of amphiphiles. Second-order phase transitions are apparently associated with the formation of two-dimensional mesophases containing the oriented OS and water molecules. The first-order phase transition can be attributed to the formation of OS crystals or mixed OS–water crystals at the interface. In the adsorption of aromatic alcohols, a mesophase is formed in second-order phase transitions, is less ordered (has a higher entropy) for a higher density of the OS, and, judging from the relaxation times of approximately 10^{-8} s, contains water molecules capable of changing their orientation as the temperature is varied. In the first-order phase transition, this mesophase is converted into two-dimensional crystals in which the OS and water molecules are linked by hydrogen bonds. According to X-ray diffraction data,[73] similar planar packing is characteristic of phenol and THB hydrates.

Manifestation of phase transitions in different relations.

Relation	Order of phase transition	
$C(E)$	jump	maximum*
$V_h(E)$	peak	zero
$\tau(E)$	jump	peak

*It may be that the finite $C(E)$ values at the maxima on the CE curve are due to the fairly large amplitudes and high modulation frequencies of the electrode potential in the measurements, while the values corresponding to thermodynamic equlibrium are singular at the transition points.

The determination by the LTJ method of the transition potentials in solutions with different OS concentrations leads to the possibility of constructing cE phase diagrams for the adsorption layers. Fig.14 presents as examples diagrams of this kind for solutions of n-pentyl alcohol and THB. For low values of c, a second-order transition from a two-dimensional solution to a water crystal (line II) occurs in the region of adsorbability. With increase in c, two second-order transitions occur in the first case, bounding the region of existence of the mesophase ($\theta \geqslant \theta_c$). On further increase in the OS concentration, first-order transitions (line I) from the mesophase to the crystal are observed. In the case of THB, the latter exists up to the maximum attainable values of c.

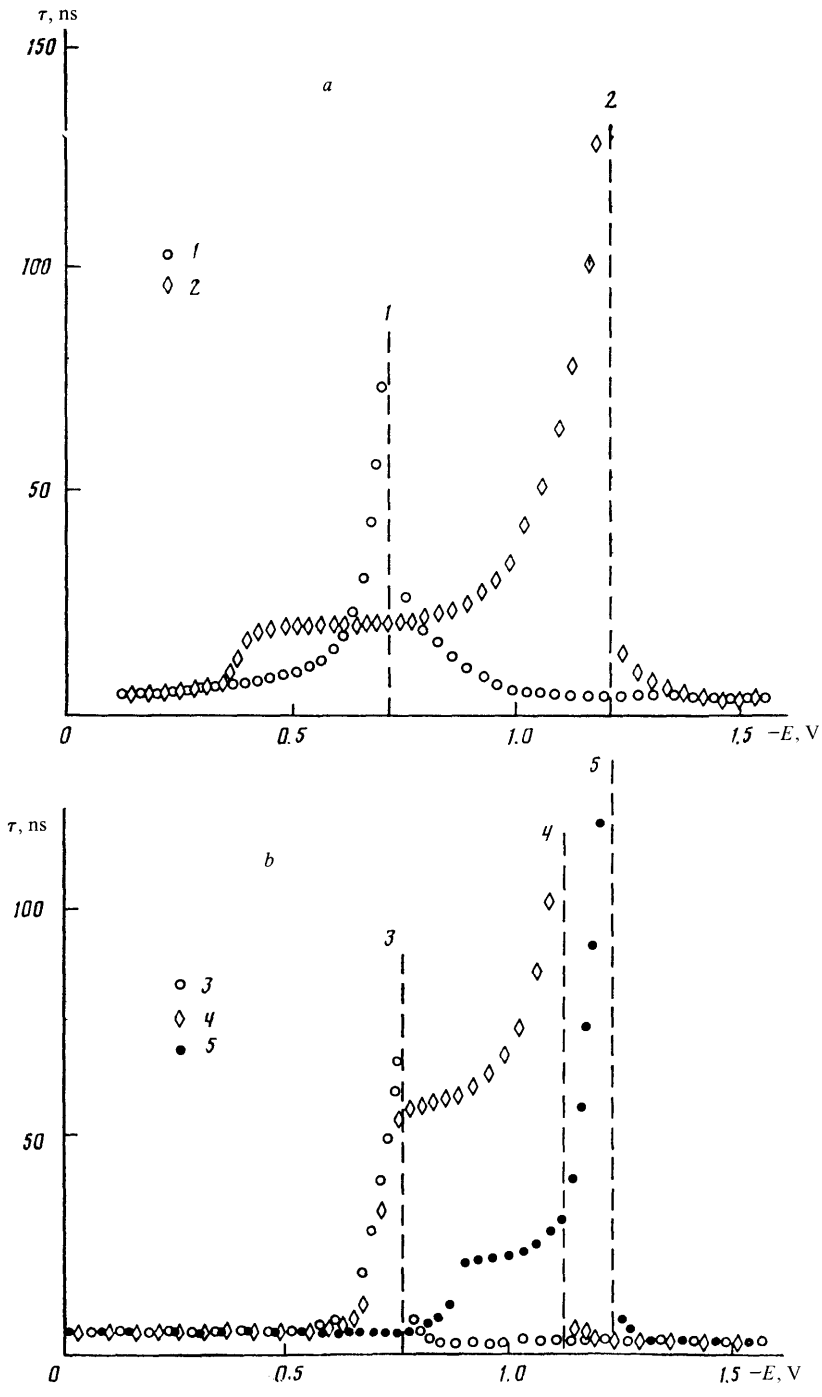


Figure 13. Characteristics EDL relaxation time for the adsorption of phenol (*a*) and 1,3,5-trihydroxybenzene (*b*) on mercury; the OS concentrations are 4×10^{-3}, 0.2, 10^{-3}, 4×10^{-2}, and 0.1 M for curves *1*—*5* respectively.[64]

Despite the limited number of examples of the application of the LTJ method, the data obtained show that the combination of the new method with the traditional procedures ensures a fairly complete thermodynamic description of the EDL both in terms of derivatives of the thermodynamic potential with respect to electrical variables and activities and in terms of temperature. The sharp changes in the relaxation times observed by the LTJ method in the regions of singularities in these derivatives display a set of different phase states of the EDL and the transitions between them of both first and second orders. Further development of this field will be associated

with the testing of structural models of two-dimensional phases and phase transitions, which can be achieved, in particular, with the aid of electroreflection spectra and IR and Raman spectroscopy. The version of LTJ developed is designed for the measurement of relaxation times within a comparatively narrow range $10^{-8}-10^{-6}$, which is known *a priori* not to include the entire relaxation spectrum of the EDL. The high thermal conductivities of metals and the possibility of changes in the duration of the laser pulses make it possible to extend the dynamic range of the LTJ (approximately to $10^{-10}-10^{-4}$ s), creating thereby the relaxation spectroscopy of the EDL.

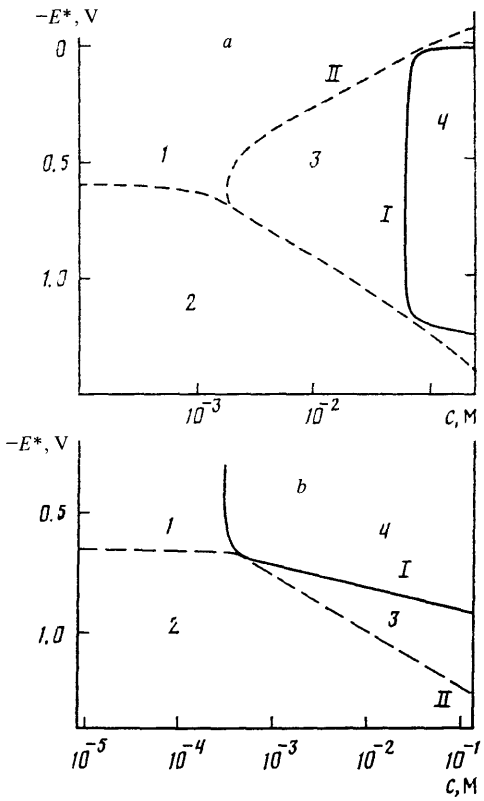


Figure 14. EDL phase diagrams for the adsorption of n-pentyl alcohol (*a*) and 1,3,5-trihydroxybenzene (*b*) on mercury; the continuous and dashed lines indicate the first- and second-order transitions respectively: 1) ice crystal; 2) OS solution in water; 3) mesophase; 4) mixed crystal of water and OS.[60,64]

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Photonics of the Triplet States of Molecular Complexes

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The review surveys the results of studies on the photophysical and photochemical reactions of triplet exciplexes and triplet-excited molecular complexes which are stable in the ground state. These two groups of excited molecular compounds are compared and the influence of the electronic structure on the kinetics and mechanisms of the elementary photoprocesses is analysed. The formation reactions and properties of the triplet exciplexes of various classes of organic substances are examined in detail.
The bibliography includes 110 references.

CONTENTS

I. Introduction 620
II. Photonics of triplet-excited electron donor-electron acceptor complexes 622
III. Triplet exciplexes 624
IV. Formation of the triplet states of molecular complexes as a result of intersystem crossing 629

I. INTRODUCTION

Many photochemical reactions—oxidation-reduction, isomerisation, addition, etc. reactions—proceed with participation of excited organic donor—acceptor molecular compounds. Complex formation keeps the reactant molecules near one another and orients them appropriately in space, thereby promoting the occurrence of the process.

Electron donor—electron acceptor (EDA) complexes or, in other words, charge-transfer complexes (CTC) are formed on charge transfer from an occupied donor orbital to an unoccupied electron acceptor orbital, which results in a decrease in the energy of the molecular system and a chemical bond is formed. According to Mulliken,[1] the molecular complex is a resonance hybrid of the so called non-bonded (AD) and ionic (A^-D^+) structures†:

$$AD \leftrightarrow A^-D^+ , \qquad (1)$$

In the hypothetical non-bonded state AD, there is no interaction between the molecules forming part of the complex. A dissociative potential surface corresponds to the complex (Fig.1). A potential surface of the bonding type corresponds to the "pure" ionic state A^-D^+. In this state, the components are held together by Coulombic attraction forces. If the structures A and D and A^-D^+ are capable of interconversion (1), then a mixed state arises and is described by the wave function

$$\psi_N = a_1\psi(AD) + a_2\psi(A^-D^+) , \qquad (2)$$

and has less energy than AD or A^-D^+. The new state has a potential surface with a minimum corresponding to the equilibrium configuration of the real complex.

In describing the excited states of molecular compounds, one must also take into account the locally excited structures—hypothetical structures without interaction between the components with the excitation localised on A or D (A^*D or AD^*):[2]

$$^1\psi_E = b_1^1\psi(AD) + b_2^1\psi(A^-D^+) + b_3^1\psi(A^*D) + b_4^1\psi(AD^*) . \qquad (3)$$

† The letter A denotes an electron acceptor molecule, D denotes an electron donor molecule, and an asterisk denotes an electronically excited species.

The contribution of each term in Eqns.(2) and (3) is determined by the energy of the corresponding state. The energies of the structures A^*D and AD^* are close to those of the corresponding excited molecules A^* and D^*. For the majority of organic CTC, the energies of the "pure" singlet and triplet charge-transfer states do not differ greatly. For gas-phase systems, they are estimated with the aid of the equation[1]

$$E(A^-D^+) = IP - EA - W$$

where IP is the ionisation potential of the electron donor, EA the energy of the electron affinity of the acceptor, and W the energy of the Coulombic interaction of the ions in the charge-transfer state. In the calculation of the energies of the structures A^-D^+ of the complexes in solutions, it is essential to take into account the solvation energy ΔH_s:

$$E(A^-D^+) = IP - EA - W - \Delta H, \qquad (5)$$

The difficulty of calculating the latter can be obviated by using the corresponding electrochemical potentials:

$$E(A^-D^+) = E_{1/2}^{ox} - E_{1/2}^{red} - W . \qquad (6)$$

Naturally, in this case $E(A^-D)$ refers to the solvent in which $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ were determined. In order to convert it into the expressions for other media, it is necessary to introduce correction terms into Eqn.(6). The Coulombic interaction energy of two molecular ions in Eqns.(4)—(6) is usually substituted by the electrostatic interaction energy of two unlike points charges (e) separated by a distance equal to the sum of the molecular radii r (usually ~0.5 nm) in a medium with a dielectric constant ε:

$$W = \frac{e^2}{\varepsilon \cdot r} . \qquad (7)$$

In more accurate calculations of the attraction energy of the ions, account is taken of the distribution of charges in space.[3]

In those cases where $E(AD) \ll E(A^-D^+) \ll E(A^*D), E(AD^*)$, the charge-transfer state is the lowest excited state of the complex. For the opposite relations $E(A^-D^+) \gg E(A^*D), E(AD^*) \gg E(AD)$, the

locally excited state is the lowest. If the energies of the locally excited and charge-transfer state are similar, their effective mixing takes place.

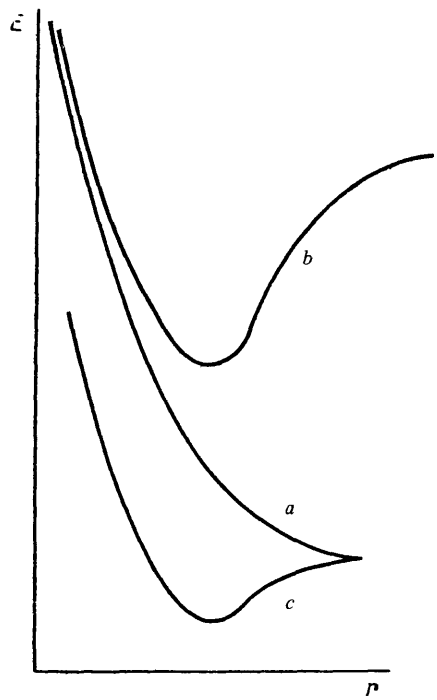


Figure 1. The potential energy (E) curves for the non-bonded state (a), the charge-transfer state (b), and the molecular complex (c); r is the distance between the species.[1]

Depending on the fraction of the charge-transfer state in the ground state, which to a large extent determines the stability of the donor–acceptor complex, it is possible to distinguish two limiting types: highly stable complexes with virtually complete charge transfer and complexes in which there is no charge transfer and no interaction of the components associated with it. Compounds of the latter group exist only at the instant of the collision of their reactant molecules (contact CTC). They are formed from the molecules of weak donors and weak acceptors.[4] Very powerful electron donors and electron acceptors give rise to complexes of the other extreme type mentioned above–radical-ion salts in which the energies of charge-tgransfer states are similar to or even lower than the energies of the non-bonding structures.[5]

The ground state of contact complexes involves repulsion for intermolecular distances corresponding to the equilibrium configurations of the molecular compounds. When the components are moved apart to a distance of approximately 0.3 nm, a small minimum appears on the potential surface for the system, which is due to relatively long-range but weak universal intermolecular forces.[6] Such van der Waals complexes have been detected and investigated with the aid of the special technique of cooled molecular beams.[7] However, in liquid solutions at room temperature, van der Waals forces are not able to ensure any appreciable stability of the molecular compounds formed on collision of the molecules of weak electron donors and weak electron acceptors.

The conversion of the contact complexes into a polar excited state greatly strengthens the bond between the components. Such donor–acceptor compounds, which exist virtually only in the excited state, have been called exciplexes or heteroexcimers.[8] Following the loss of the electronic excitation energy, the exciplexes pass to a state with a dissociative potential surface and decompose. As a consequence of the large difference between the energies $E(A^-D^+)$ and $E(AD)$, in exciplexes, in contrast to the excited CTC, there is no interaction between the structures AD and A^-D and the stabilisation of the ground state induced by such interaction is lacking (Fig.2).

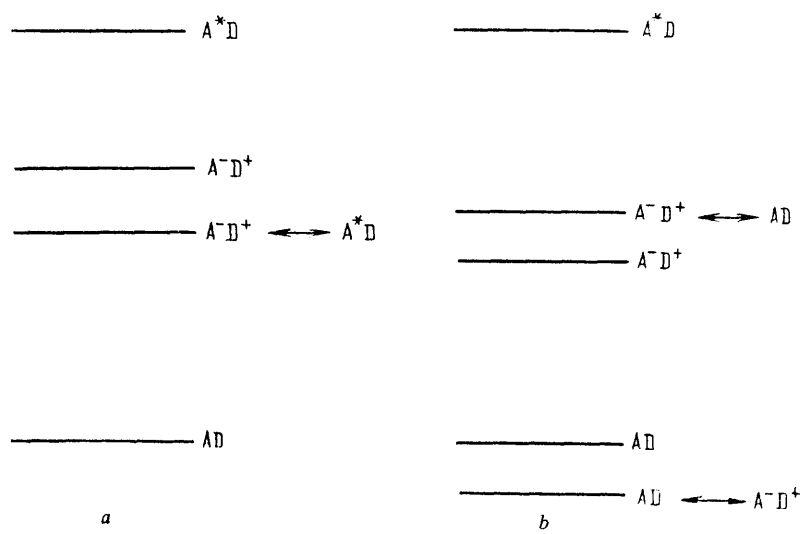


Figure 2. The energy level scheme for exciplexes (a) and CTC (b).

The rule of overall spin conservation of the system holds in electron exchange. Charge-transfer triplet states do not therefore interact with the AD state and the term containing AD does not enter into the expression for the wave function for the triplet-excited molecular state $^3\psi_E$:

$$^3\psi_E = c_1^3\psi(A^*D) + c_2^3\psi(A^-D^+) + c_3^3\psi(AD^*) \quad . \qquad (8)$$

Thus the triplet states of both exciplexes and CTC are not perturbed by the interaction with the non-bonded state AD. From this point of view, there are no differences between the triplet-excited EDA compounds, which are stable in the electronic ground state, and the triplet exciplexes. The study of both groups of molecular complexes yields mutually complementary information.

The excited CTC can be obtained on direct photoexcitation of molecular compounds:

$$AD \xrightarrow{h\nu} {}^1(A^{\delta-}D^{\delta+})^* \rightsquigarrow {}^3(A^{\delta-}D^{\delta+})^* \quad .$$

In liquid solutions, complex formation reactions also take place between excited and unexcited molecules

$$^1A^* + D \rightleftarrows {}^1(A^{\delta-}D^{\delta+})^* \quad ,$$
$$^3A^* + D \rightleftarrows {}^3(A^{\delta-}D^{\delta+})^* \quad .$$

Both complexes with a dissociative ground state and molecular compounds, which are fairly stable in the unexcited form, are formed via a dynamic pathway.

Systematic studies on the photonics of molecular compounds have been carried out since the beginning of the 1950's. Initially organic CTC having a stable ground state were investigated.[8-11] The study of Leonhard and Weller[12] initiated an avalanche of publications devoted to singlet exciplexes. The triplet exciplexes, discovered at the beginning of the 1970's,[13,14] have been studied much less than the singlet exciplexes. This is due to the complexity of their experimental detection and investigation: in liquid solutions, the triplet exciplexes do not as a rule luminesce. These excited compounds evidently play an important role in many photochemical processes. Their photophysical properties differ significantly from those of the singlet exciplexes. The insufficiency of experimental data is fully compensated by data obtained in studies on CTC. As already stated, the electronic structures of the triplet exciplexes and triplet-excited EDA complexes are identical, which makes it possible to construct an integral picture of this important group of excited species on the basis of seemingly unrelated facts.

II. PHOTONICS OF TRIPLET-EXCITED ELECTRON DONOR–ELECTRON ACCEPTOR COMPLEXES

1. Luminescence-spectroscopic Properties

The phosphorescence spectra of molecular complexes, whose triplet state is locally excited, are very similar to the corresponding spectra of the "free" electron acceptors or donors. An example of such molecular compounds is provided by the complexes of trinitrobenzene, tetracyanobenzene, and tetrachlorophthalic anhydride with aromatic hydrocarbons – benzene, toluene, and naphthalene.[16-19]

Detailed analysis of the phosphorescence spectra[16-19] nevertheless reveals distinctive features of the complex formation. For example, the vibrational structure of the phosphorescence spectra of the CTC is more closed compared with the phosphorescence spectra of the corresponding components and furthermore vibrations with lower frequencies are manifested in them.[18] In many cases a small but nevertheless appreciable bathochromic shift of the phosphorescence spectra of the electron donor, depending on the donor–acceptor parameters of the components of the EDA complexes, is observed.[18] For example, the 0–0 transition in the phosphorescence of naphthalene occurs in the region of 21.3×10^{-3} cm^{-1}, while for the complex of naphthalene with dichloro-*o*-phthalic anhydride it occurs in the region of 21.37×10^3 cm^{-1} (Table 1).

Table 1. The positions of the bands ($\tilde{\nu}_{phosph}$) and the phosphorescence quenching times (τ_{phosph}) for the EDA complexes of naphthalene in frozen solutions.

Electron acceptor	Solvent	$\tilde{\nu}_{phosph}$, 10^{-3} cm^{-1}	τ_{phosph}, s	Refs.
Dichloro-*o*-phthalic anhydride	PEI	21.37	2.1	[26]
Tetrachloro-*o*-phthalic anhydride	PEI	21.3	1.65	[26]
Tetrabromo-*o*-phthalic anhydride	PEI	21.2	0.29	[26]
Pyromellitic anhydride	n-propyl ether	21.3	1.8	[23]

Note: PEI is a 3 : 1 mixture of isopropyl ether and isopentane.

The lifetimes of the phosphorescent locally excited states of molecular complexes are usually shorter than the lifetimes of the corresponding states of the "free" components of the CTC,[16-18] which may serve, together with spectroscopic data, as evidence for complex formation. However, if the acceptor contains no heavy atoms, then complex formation does not affect greatly the phosphorescence lifetimes. As for the usual organic molecules, the introduction of heavy atoms into the complex shortens appreciably the duration of the phosphorescence.[20]

Thus the electronic transitions in the locally excited triplet states of molecular compounds can be regarded as electronic transitions perturbed by complex formation and occurring in the photoexcited component. Complex formation intensifies the spin–orbit coupling, which fixes in its turn the single S_1 and the triplet T_0 states, and the radiative transitions to the ground state $S_1 \rightarrow S_0$ and $T_0 \rightarrow S_0$.[21] This results in the acceleration of intersystem processes, which is manifested by a shortening of the lifetimes of the phosphorescent states of the photoexcited components.

The triplet–triplet absorption spectra of the CTC of this group resemble the triplet–triplet absorption spectra of the corresponding "free" CTC components. However, in these spectra too one can observe distinct features of complex formation—the broadening of the absorption bands and the appearance in the long-wavelength part of the spectrum of bands due to charge transfer from the excited triplet state localised on one of the components to the unoccupied level of the electron acceptor.[22]

Complexes with the lowest triplet charge transfer states have completely different phosphorescence spectra. These spectra consist of structureless bands due to reverse charge transfer, whose maxima undergo a hypsochromic shift with increase in the electron affinity of the acceptor.[16-19] The duration of the phosphorescence of the EDA complexes of this group is shorter, as for the previous

group, then the duration of the phosphorescence of the "free" component with the lowest triplet state energy when this is closest to the energy of the triplet state of the complex.[23] The shortening of the phosphorescence lifetime as a result of complex formation is caused, according to Hayashi et al.,[23] by a change in the rates of both radiative and non-radiative transitions.

The triplet–triplet absorption spectra of complexes of this group have been studied in detail in relation to the CTC of tetracyanobenzene with durene and hexamethylbenzene.[25] The absorption spectra of molecules in the charge transfer state do not resemble the triplet–triplet absorption spectra of the "free" components. They manifest electronic transitions involving reverse charge transfer and transitions leading to locally excited states of the ion:[25]

$$A^-D^+ \begin{cases} \longrightarrow AD^* \\ \longrightarrow A^{-*}D^+ \\ \longrightarrow A^-D^{+*} \end{cases}$$

The triplet locally excited complexes and the triplet complexes in the state involving virtually complete charge transfer between the components can be regarded as corresponding to extreme points in the series of excited complexes in which the degree of charge transfer can vary from 0 to 100% depending on the nature of the reactants. The change in the degree of polarity of the excited CTC influences strongly the luminescence-spectroscopic properties. As the degree of charge transfer is altered, the lifetimes and the positions of the phosphorescence bands change, and the absorption bands of the triplet-excited complexes are displaced.[2,23–25] These effects are strongest when the degree of charge transfer exceeds 50%.[24]

2. Dissociation of Triplet-Excited CTC into Ions

The products of the total electron transfer can be formed on dissociation of both singlet- and triplet-excited EDA complexes. Each of these mechanisms has its specific features.

The degree of involvement of states of different multiplicity in ionic dissociation processes of the CTC is determined in the first place by the thermodynamic conditions. In solvents with a high dielectric constant ε, the energy of the charge-transfer state is close to the energy of the state with dissociated ions. The EDA complexes in the charge-transfer state can therefore dissociate into free ions in highly polar solvents. On the other hand, locally excited complexes are unable to decompose spontaneously into ions.

The numbers of the free radical-ion species formed on dissociation of singlet- and triplet-excited states are determined by the rates of internal conversion, ionic dissociation, and intersystem processes involving the formation and deactivation of triplet states. However, the kinetics of these reactions have been scarcely investigated.

It is usually regarded as fully demonstrated that radical-ions are formed as a result of the dissociation of the triplet-excited CTC if the test system satisfies the following features.

1. The increase in the concentration of the radical-ion products occurs in the microsecond range parallel to the decrease in the intensity of the phosphorescence or the triplet–triplet absorption. For example, the photoexcitation in the charge transfer band of the complex of tetracyanobenzene with tetrahydrofuran in dichloroethane is accompanied by the formation of the radical-ion of the electron acceptor in the course of 300 μs. The time during which the concentration of the products of the ionic dissociation of the CTC increases then corresponds to the quenching time of the phosphorescence of the complex.[27]

2. Oxygen is an effective quenching agent for triplet states[21] and the yield of the products of the ionic dissociation of the triplet-excited CTC therefore diminishes as the solutions are saturated with oxygen. However, in the analysis of the influence of oxygen on the formation of radical-ion species it is essential to take into account the fact that this criterion is less rigorous, because oxygen can also quench a singlet-excited state and can accelerate intersystem crossing. For this reason, the data concerning the influence of oxygen on the yields of the radical-ions formed on photoexcitation of CTC require in general a careful kinetic analysis.[28]

3. If the radical-ion species arise as a result of the dissociation of the CTC in the triplet state, then the introduction into the solution of sensitisers, which are capable, after the transition to the triplet state, of transferring their energy to the complexes and of exciting their triplet states, increases the yield of the products of the total electron transfer.[29,30]

The triplet mechanism of the formation of radical-ion species operates only in the case of complexes whose lowest triplet states are charge-transfer states. The complexes of tetracyanoethylene, tetracyanobenzene, and pyromellitic dianhydride with π- and *n*-type electron donors, such as mesitylene, α-methylstyrene, dioxan, tetrahydrofuran, etc. serve as examples.[29,30]

If the lowest triplet states of the CTC belong to the class of locally excited states, then the ionic dissociation of the triplet-excited complexes does not take place. However, even in this case radical-ions may be formed following the absorption by the triplet-excited complexes of a second light quantum,[34–36] which converts the complex into a high-lying charge-transfer state:

$$AD \xrightarrow{h\nu} {}^1(AD)^* \rightarrow {}^3(A^*D) \xrightarrow{h\nu} {}^3(A^-D^+)^* \rightarrow A^- + D^+ .$$

Two-quantum CTC photodissociation processes have been observed experimentally from the quadratic dependence of the yield of radical-ions on the intensity of the exciting light. Analysis of such relations shows that the photoreaction of the complexes of tetracyanobenzene, pyromellitic and tetrachlorophthalic anhydrides with ether proceeds via a two-quantum mechanism, while the reaction of the complexes of the same acceptors with methyltetrahydrofuran, which is a stronger electron donor, involves a one-quantum mechanism.[35] In both the former and the latter group of complexes, the lowest triplet states belong to the locally excited type. The characteristics of the photochemical behaviour of molecular compounds of the first group are determined by the fact that in their molecules the first singlet excited states belong to the class of locally excited states. The dissociation of such molecular compounds is possible only after excitation to high-lying charge-transfer states.

Cases where both singlet- and triplet-excited states of EDA complexes are charge-transfer states are of considerable interest. As already stated, the energies of these compounds are similar and radical-ions can therefore form on dissociation of the CTC in either state. However, this most complex case has been scarcely investigated. It is only known that the relative efficiencies of the singlet and triplet channels leading to the formation of the products of the total electron transfer depend on the polarity of the medium. For example, in moderately polar solvents, the ionic dissociation of excited CTC of tetracyanobenzene and pyromellitic-dianhydride with ether, dioxan, and tetrahydrofuran takes place after the conversion of the complex to the triplet state, while in highly polar solvents—acetonitrile and butyronitrile—it occurs as a result of the decomposition of the singlet-excited CTC.[33]

III. TRIPLET EXCIPLEXES

The interaction of the triplet molecules of porphyrins, carbonyl compounds, dyes, and compounds of other classes with electron donor or electron acceptor molecules results in the formation of excited intermediates, which are frequently referred to in the literature as triplet exciplexes. Nevertheless, these excited molecular compounds are in essence triplet-excited CTC, which have a bonding ground state. This is manifested by the fact that the components of the majority of the so-called triplet exciplexes in the electronic ground state are capable of reacting with one another to form relatively stable molecular compounds. Specific examples will be given below. The application of the term exciplex to triplet-excited CTC is justified, because these excited species are formed via a dynamic mechanism, like the "true" exciplexes. Furthermore, the triplet states of both groups of molecular compounds are not perturbed as a result of the interaction with the non-bonded state.

1. Triplet Exciplexes of Porphyrin Compounds

The tetrapyrrole pigments undergoing reversible oxidation-reduction reactions in the cells of living organisms fulfil a series of key functions in photobiological processes. Studies under model conditions, including solutions and photochemical oxidation-reduction reactions with participation of tetrapyrrole pigments of all types—porphyrins, phthalocyanines, chlorines, etc.—have therefore developed widely.[38] The triplet states of the pigments play the main role in these photoreactions,[39] which is due to the long lifetime of the triplet states of many porphyrin compounds, the high quantum yields of the intersystem crossing, the pronounced electron-donating properties of the triplet-excited molecules, and the spin rules prohibiting the recombination of the primary radical-ion pairs formed. The interaction of the triplet molecules of the tetrapyrrole pigments with electron donors or acceptors shortens the lifetime of the triplet molecules and leads to the formation of "free" products of the total electron transfer in polar media.[38,39] In non-polar solvents, quenching may be accompanied by the appearance of triplet exciplexes.

The formation of a triplet exciplex was first observed in a study[13] in which the products of the pulse excitation of the solution of Zn-tetraphenylporphin in benzene containing *p*-benzoquinone were investigated. As a result of the action of the light pulse in this system, a variable absorption appeared, the kinetics of the disappearance of which were described by a complex two-component curve. It was suggested[13] that one of the components describes the destruction of a triplet exciplex. Subsequently analogous data were obtained in the study of the interaction of the triplet molecules of certain other porphyrins,[14,40-42] phthalocyanines,[42] and chlorophyll[43,44] with electron acceptors.

The hypothesis of the formation of triplet exciplexes on quenching of the triplet states of porphyrin molecules by electron acceptors has been confirmed by the study of the absorption spectra of the intermediates and of their deactivation by energy acceptors, in the study of the slow fluoroescence and pulse photoconductivity of the solutions, and by careful analysis of the kinetic curves.

It has been established[40] that the absorption spectrum of the "long-lived" component of the kinetic curve differs appreciably although not very greatly from the absorption spectra of triplet molecules. The spectra of these intermediates differ also from the absorption spectra of the corresponding radical-ions. The lifetime of the intermediate species shortens after the introduction into the solution of oxygen, azulene, tetracene, and perylene—substances whose molecules have low energies of the triplet states and which can therefore serve as energy acceptors in relation to the triplet porphyrin exciplexes. The rate constants for the quenching of the triplet exciplexes via these substances are close to the diffusion rate constants. The formation of the triplet chlorophyll exciplexes by reaction with organic electron acceptors is accompanied by the appearance of a slow fluorescence, whose spectrum agrees with the well known fast fluorescence spectrum of chlorophyll.[43,44] The appearance of the slow fluorescence in solutions where there are virtually no free triplet chlorophyll molecules can be caused only by processes involving triplet exciplexes. When electron acceptors are added to weakly polar chlorophyll solutions at concentrations sufficient for the complete quenching of the triplet states, an increase in photoconductivity is not observed.[40]

The triplet exciplexes of porphyrin compounds can be regarded as locally excited complexes with a relatively small contribution by the state involving charge transfer from the porphyrin to the oxidant. This is indicated by the absorption spectra of the complexes, which resemble the absorption spectra of the corresponding porphyrins in the triplet state.[40,42-44] This fact may at first sight appear to be unexpected because porphyrins are powerful electron donors.[45] However, together with very pronounced electron-donating properties, porphyrins are characterised by low energies of the triplet states (~ 150 kJ mol^{-1}),[38] so that the lowest triplet state of the EDA complexes of porphyrins with many electron acceptors is a locally excited state.

The contribution of the wave functions of the polar states to the wave function of the excited complex depends on the nature of the reactants, as stated above. With increase in the electron-accepting capacity of the oxidant forming part of the exciplex, the absorption spectrum of the latter becomes increasingly different from the absorption spectrum of the triplet molecules and begins to resemble increasingly the absorption spectrum of the corresponding radical-cation.[46] Even in the case of powerful electron acceptors such as dinitrobenzenes and dinitronaphthalenes, the absorption spectrum of the exciplex nevertheless differs from that of the corresponding radical-cation. Naturally, bands resembling the absorption bands of the radical-anions should also be present in the absorption spectra of the exciplexes. Owing to their low intensity, they are masked by the bands of the radical-cation.

The conclusion that the lowest triplet states of the exciplexes of many tetrapyrrole pigments formed by reaction with electron acceptors have a predominantly locally excited character has been confirmed by thermodynamic calculations.[47] Thus in non-polar media the energy of the triplet state of chlorophyll is lower than the energy of the triplet charge-transfer states of its complexes with nitrobenzene, dinitrobenzene, and *p*-benzoquinone. The triplet chlorophyll exciplexes are therefore locally excited complexes with a small admixture of the charge-transfer state.

With increase in solvent polarity, the energy of the charge-transfer state diminishes owing to its stabilisation by the dipoles of the medium. As a result of this, the formation of radical-ions becomes easier in highly polar solvents than that of exciplexes, which has been confirmed by flash photolysis data: the photoexcitation of solutions of chlorophyll and organic oxidants in highly polar media leads to the formation of a high yield of chlorophyll radical-cations with a characteristic absorption spectrum.[38,39,47]

The inversion of the levels of the locally excited state and the charge-transfer state can occur also without a significant change in solvent polarity after the introduction into non-polar solutions of

polar additives, which are capable of solvating selectively the exciplexes, inducing a decrease in the energy of the charge-transfer states. As an example, one may quote the results of a study[48] in which the influence of added ethanol, acetonitrile, and *N*-methylformamide on the lifetimes and spectroscopic properties of the triplet exciplexes of Zn-aetioporphyrin I with *p*-nitrotoluene was investigated. It was found that the presence of *N*-methylformamide in the solution at a concentration of 0.01 M shortens greatly the lifetime of the triplet exciplex. The increase in the concentration of the additive to 0.02 M is accompanied by the appearance in the spectrum of the variable-absorption bands of the radical-cations. Since such low concentrations of polar substances hardly increase the dielectric constant of the medium, the formation of free radical-ions in these solutions is therefore unlikely. The spectral changes can be explained by the inversion of the energy levels of the locally excited state and the charge-transfer state.

It has also been observed[49] that the quenching of the photo-induced absorption of chlorophyll solutions containing an electron acceptor has two-component kinetics. However, the authors of the above publication were not able to detect any intermediate products with a lifetime greater than 20 ns on interaction of the triplet molecules of the zinc complexes of porphyrins with *p*-benzoquinone and *p*-dinitrobenzene.[49,50] This served as a basis for the conclusion that the kinetic and spectral changes, explained by the formation of triplet exciplexes, are in fact due to the presence of impurities in the specimens consisting most probably of the metal-free pigments. It has to be said that, with the aid of the traditional methods of purification, it is easy to obtain spectroscopically pure preparations of tetrapyrrole pigments in which the content of the main substance is greater than 99.5%. Since metalloporphyrins have characteristic absorption spectra, it follows that extraneous coloured substances can be readily detected spectroscopically. The problem of the genesis of the two-component curves described can be solved by careful analysis of the kinetic curves. This problem will be considered in the next Section. It is possible to identify tentatively the causes of the failure of Renge and co-workers[49,50] to detect the triplet exciplexes of zinc-porphyrins with oxidants. It may be that the solvents or the metalloporphyrins themselves contained polar impurities capable of quenching the exciplexes via the mechanism considered by Roy and Whitten.[48] This may be promoted by the tendency of metalloporphyrins to form complexes.

2. Kinetics of the Quenching Processes with Participation of the Triplet Exciplexes of Porphyrin Compounds

The interaction of triplet-excited porphyrin molecules with electron acceptors is described, like the reactions of the singlet-excited molecules of aromatic substances, by a kinetic scheme which takes into account the possible occurrence of induced quenching—a process first proposed by Nakashima et al.[51] and Kuz'min and Sadovskii[52]—in parallel with the formation of exciplexes:

$$D^* + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AD)^* \xrightarrow{k_2} D + A \ , \qquad (9)$$

$$D^* + A \xrightarrow{k_4} D + A \ , \qquad (10)$$

$$D^* \xrightarrow{k_3'} D \ . \qquad (11)$$

The standard formal kinetic treatment of this scheme shows[41,42,46] that, subject to the condition $[A] \gg [D^*]$, the time variations of D^* and $(AD)^*$ are described by

$$[D^*] = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \ , \qquad (12)$$

$$[(AD)^*] = b[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \ . \qquad (13)$$

Since the absorption spectra of both components of the kinetic curve usually overlap, the overall absorption is recorded under the conditions of flash photolysis:

$$D = D_t + D_e = \epsilon_t l[D^*] + \epsilon_e l[(AD)^*] = F_1 \exp(-\lambda_1 t) + F_2 \exp(-\lambda_2 t) \ . \qquad (14)$$

In Eqns.(12)–(14), we have

$$\lambda_{1,2} = B/2 \pm (B^2/4 - C)^{1/2} \ ,$$

$$B = k_2 + k_{-1} + (k_1 + k_4)[A] = \alpha + \beta[A] \ ,$$

$$C = k_3(k_2 + k_{-1}) + (k_1 k_4 + k_2 k_4 + k_{-1} k_4)[A] = \gamma + \delta[A] \ ,$$

where ϵ_t and ϵ_e are the molar extinction coefficients of the triplet molecules and exciplexes respectively and l is the length of the cuvette. The pre-exponential factors a_1, a_2, b, F_1 and F_2 can be found by the usual procedures from the initial conditions.[46] In Eqn.(14), D_e and D_t are the optical densities due to the absorption of the triplet-excited molecules and the triplet exciplexes.

The lifetimes of the triplet exciplexes τ_e can be found from the dependence of λ_2 on the concentration of the quenching agent A:[42]

$$1/\tau_e = \lambda_{lim} = \lim_{[A]\to\infty} \lambda_2 = k_2 + k_{-1}k_4/(k_1 + k_4) \qquad (15)$$

Eqn.(15) shows that the deactivation of the triplet exciplex can take place in two ways: via the direct intersystem degradation of the electronic excitation energy and as a result of the dissociation of the exciplex with subsequent deactivation of the triplet molecules induced by the quenching agent. The efficiency of each of these channels is characterised by the corresponding terms of Eqn.(15).

If the quenching process proceeds via a state involving the formation of an intermediate excited complex, then it follows from Eqns.(12)–(14) and (1), over a wide range of quenching agent concentrations, the dependences of λ_1 and λ_2 on [A] do not obey the Stern–Volmer equation,[42] which can be written in the form

$$\lambda_{1,2} = \frac{1}{\tau_0} + k_q[A] \ ,$$

where k_q is the quenching rate constant, and (2), as the quenching agent concentration is varied, the intensities of the first and second components of the kinetic curve vary in such a way that $A_1 + A_2 = \text{const}$.[46]

For systems where $k_4 \ll k_1$, the lifetimes of the triplet exciplexes of porphyrins with electron acceptors hardly differ from the lifetimes of the triplet molecules of the corresponding porphyrins in liquid degassed solutions.[42,53] The latter is entirely understandable, because the processes leading to the deactivation of the localy excited complexes can be regarded, as stated above, as weakly perturbed electronic transitions in the photoexcited component of the exciplex. If the rate of deactivation of the locally excited component is high, for example, as a consequence of the spin–orbit coupling, then the lifetime of the corresponding locally excited exciplex is short. Exciplexes of the ruthenium complexes of phthalocyanine with certain organic electron acceptors can serve as confirmation of this.[54] Depending on the axial ligand, the lifetimes of the triplet molecules of the "free" metallophthalocyanine range from 0.43 to 0.32 μs, while the lifetimes of the exciplexes range from 0.77 to 0.18 μs. Like the majority of the exciplexes examined above, these exciplexes are characterised by a low contribution of the charge transfer states. It is of interest that in certain cases the lifetime of the exciplex of the ruthenium complex of phthalocyanine was several times longer than the lifetime of the triplet molecules under the same conditions, which can be explained by the change in the rates of the non-radiative transitions as a result of complex formation.

If the second term in Eqn.(15) is sufficiently large compared with the first, then the lifetimes of even locally excited exciplexes can depend on the nature of the oxidant involved in the complex formation. The data in Table 2, which presents the values of λ_{lim} found from the dependences of λ_2 and τ_e on the oxidant concentration, serve as an illustration of this finding. In the table, the quenching agents are arranged in order of weakening electron accepting properties, while the porphyrins are arranged in order of weakening electron-donating properties. It can be seen that, for each metalloporphyrin, exciplexes with both strong and weak electron acceptors can have high values of λ_{lim}. The values of λ_{lim} which do not differ greatly from the rate constants for the pseudounimolcular deactivation of triplet porphyrin molecules ($\sim 10^3$ s^{-1}) lie in an intermediate region. The lifetimes of such triplet exciplexes, like those of the majority of triplet molecules,[9,21] are determined by the rates of quenching by residual oxygen, impurities, and the solvent. The region of long-lived exciplexes is differentiated in Table 2, an arbitrary boundary being designated by a dashed line.

Table 2. The rate constants for the deactivation of the triplet exciplexes (10^{-3} λ_{lim}, s^{-1}) of metalloporphyrins with electron acceptors in toluene solutions.[53,56]

Quenching agent	TPPMg	TPPAlOH	TPP GaOH	PhcMg	PhcAlCl	TPPInOH
2,5-Dichloro-*p*-benzoquinone	—	6.2	—	—	—	—
2,4,7-Trinitrofluorenone	1.1	10	—	—	—	10
Chloro-*p*-benzoquinone	2.2	4.2	—	—	—	—
Picryl chloride	1.2	—	12	—	—	7.2
p-Benzoquinone	2.1	1.2	—	5.8	4.8	
Toluquinone	1.8	1.5	—	7.7	3.1	15
1,4-Naphthoquinone	—	1.1	—	2.2	1.5	14
9,10-Phenanthrenequinone	—	1.0	—	—	—	—
2,6-Di-*t*-butyl-*p*-benzoquinone	1.9	0.7	—	3.6	—	30
o-Dinitrobenzene	1.0	1.2	1.2	—	—	8.2
Trinitrotoluene	—	—	0.9	—	—	—
Duroquinone	1.4	1.2	—	—	—	—
m-Dinitrobenzene	—	—	1.2	—	—	—
o-Chloronitrobenzene	1.2	—	4.5	—	—	—
o-Nitrotoluene	2.9	—	13	—	—	—
3-Nitro-*o*-xylene	4.3	—	—	—	—	—
NN-Dimethyl-*p*-nitroaniline	4.7	—	—	—	—	—

Note: TPP = mesotetraphenylporphin and Phc = tetra-t-butylphthalocyanine.

The size of the region of reduction potentials of the quenching agent $E_{1/2}^{red}$ for which low values of λ_{lim} are observed ($\sim 10^3$ s^{-1}) is determined by the electron-donating properties of the porphyrin. The tabulated data show a tendency towards a narrowing of the region of long-lived exciplexes as the electron-donating capacity of the excited molecules diminishes. The greatest number of long-lived exciplexes are therefore formed by the magnesium complex of mesotetraphenylporphin—one of the metalloporphyrins with the most pronounced electron-donating properties.

The complex dependence of the rate of deactivation of triplet exciplexes on the reduction potential of the quenching agent described above can be explained by the fact that the triplet exciplex can be deactivated not only by direct intersystem degradation but also as a consequence of dissociation with subsequent quenching agent-induced deactivation of the triplet-excited molecules formed. The relative efficiencies of these channels are determined by the ratios of the constants for the formation of the triplet exciplex, the induced quenching, and dissociation. This problem has been analysed in detail.[53,55]

In systems which exist in regions along the boundary of the "peninsula" (Table 2) of the long-lived exciplexes, we have $k_4 \gtrsim k_1$ [53] and therefore the two terms of Eqn.(15) are comparable and both mechanisms of the deactivation of triplet molecules described are important in the description of the process.

The size of the quenching agent concentration range in which distinct two-component quenching curves are observed depends on λ_{lim}. For systems with high λ_{lim}, the quenching times for the first and second components of the kinetic curve can remain close to one another even if the concentration of the quenching agent changes appreciably (by several orders of magnitude). Bearing in mind also that the intensity of the first component diminishes with increase in the concentration of the quenching agent, the kinetics of the disappearance of the induced absorption in such systems remain virtually monoexponential over the entire accessible range of variation of the quenching agent concentration. In this case, the process proceeds in a quasi-stationary manner. The characteristic time of such a curve varies with increasing quenching agent concentration in accordance with a hyperbolic law:[53]

$$1/\tau = \frac{\alpha + \beta [A]}{\gamma + \delta [A]} , \qquad (16)$$

tending to the limiting value defined by Eqn.(15).

In a study of systems which are remote from the peninsula of the long-lived exciplexes, the formation of triplet-excited complexes cannot be observed by kinetic methods. Evidently the exciplexes in such systems have such short lifetimes that the dependence of $1/\tau$ on [A] becomes linear over the entire accessible range of quenching agent concentrations. Such short lifetimes of the triplet exciplexes can be caused solely by high dissociation and deactivation rate constants, because even for systems in the boundary regions the ratio $k_4/(k_1 + k_4)$ does not differ greatly from unity—its maximum value.

The hyperbolic form of the relation between $1/\tau$ and [A] [Eqn.(16)] can be explained by the fact that, with increase in the quenching agent concentration, the equilibrium in the exciplex formation reaction (9) shifts towards the excited complex. Such relations can be regarded as evidence for the reversible formation of the excited complexes when triplet molecules are quenched.[56,57] The equilibrium character of the formation by triplet-excited molecules of complexes with the quenching agent was observed in a study of the quenching of the triplet-excited states of the palladium complex of mesotetraphenylporphin by *NN*-dimethylaniline in liquid degassed solutions.[58] It has to be said that Pd-porphyrins have the fairly rarely encountered property of an intense phosphorescence in liquid deaerated solutions.[38] In a study of the quenching of the above system, characteristic negative deviations from the linear Stern–Volmer relation, associated with the formation of triplet exciplexes, were observed. Calculations showed that the equilibrium stability constant of the triplet exciplex of the above porphyrin with *NN*-dimethylaniline is approximately 10 litre mol^{-1}.[58] It is of interest that Mercer-Smith et al.[58] failed to observe a change in the phosphorescence spectra of the porphyrin after the introduction of an amine into the solution, which can be due to the fact that the triplet exciplex does not phosphoresce or, if it does phosphoresce, then it is locally excited. As already stated, the spectra of such complexes are virtually identical with the spectra of the corresponding components.

Being in the ground state, the molecules of the porphyrins and the electron acceptors can form relatively stable molecular complexes with one another.[58] Taking this factor into account, the majority of

the triplet exciplexes considered in the present Section should be included among excited EDA complexes, using the terminology proposed in the introductory Section. In the triplet-excited state, organic CTC are much more stable than in the ground state: the corresponding equilibrium constants for the excited states are 3 – 5 orders of magnitude greater than for the ground state.[42,46,60] The above triplet exciplexes are much more stable than the stable highly polar singlet exciplexes of aromatic compounds with oxidants or reductants.[61,62]

The high stability of the triplet exciplexes of porphyrins is somewhat unexpected, because, like other locally excited complexes, they cannot have high enthalpies of formation. Charge transfer stabilises them only slightly. The exciton interaction is also negligibly weak, because the energy of the triplet state of porphyrin is smaller by at least 100 kJ mol^{-1} than the energies of the lowest triplet states of the electron acceptors listed in Table 2.

The high stability of the triplet exciplexes is due to their high positive entropies of formation,[60,63] whose origin can be accounted for by a change in the structure of the solvation shells of the reactant molecules. The thermodynamic parameters of the exciplexes satisfy the following general compensation relations regardless of their multiplicity[60,63] (Fig.3):

$$\Delta H = \Delta H_0 + \beta_K \Delta S \ , \qquad (17)$$

where ΔH and ΔS are the enthalpy and entropy of the complex formation reaction, ΔH_0 = –17.7 kJ mol^{-1}, and β_K = 244 K. In plotting Fig.3 and in the calculation of the parameters of Eqn.(7), use was made of virtually all the literature values of ΔH and ΔS for excited complexes known to us. For exciplexes, the isoequilibrium temperature β_K is much lower than the isoequilibrium temperature for donor-acceptor complexes in the electronic ground state, which has been stated[64] to be 337 K. This may indicate that the excited complexes differ from the unexcited ones by a greater sensitivity of the structure to changes in the interaction energy. According to Lefler,[65] where there is a linear relation between ΔH and ΔS, the Gibbs free energy of the chemical reaction ΔG is expressed by the equation

$$\Delta G = \Delta H_0 - (T - \beta_K)\Delta S \ .$$

Since the isoequilibrium temperature for exciplexes lies below room temperature at which the stability constants are usually measured, the transition to more positive ΔS is accompanied in changes in ΔH, which increase the stability of the complex.

The rate constants for the formation of triplet exciplexes of porphyrin compounds with electron acceptors increase with increase in the reduction potential of the quenching agent and reach the diffusion region, where k_1 is almost independent of the nature of the oxidant.[53,66] The slope of the "vertical" branch of the relation between k_1 and the reduction potential of the oxidant is close to $-1/RT$, which is a characteristic feature of electron transfer processes, although the reaction leads to the formation of a locally excited complex with a small admixture of the charge-transfer state. In order to account for this contradiction, it has been suggested[53,66] that the formation of the exciplex involves an electron transfer stage. the entire process can be described by the scheme

$$\underset{\text{collision complex}}{D^* + A \rightleftarrows D^* \cdots A} \rightleftarrows \underset{\text{radical-ion pair}}{D^{\dot{+}} \cdots A^{\dot{-}}} \rightleftarrows \underset{\text{exciplex}}{(AD)^*} \rightarrow D + A \ .$$

After the mutual approach of the reactant molecules through diffusion, an electron is transferred with formation of the primary radical-ion pair. The species then continue to approach one another under the influence of Coulombic forces. This is accompanied by the partial neutralisation of the charges and the solvation environment and the mutual orientations of the molecules in the solvent cage are rearranged. This in fact results in the appearance of structures responsible for the high stability of the triplet exciplexes.

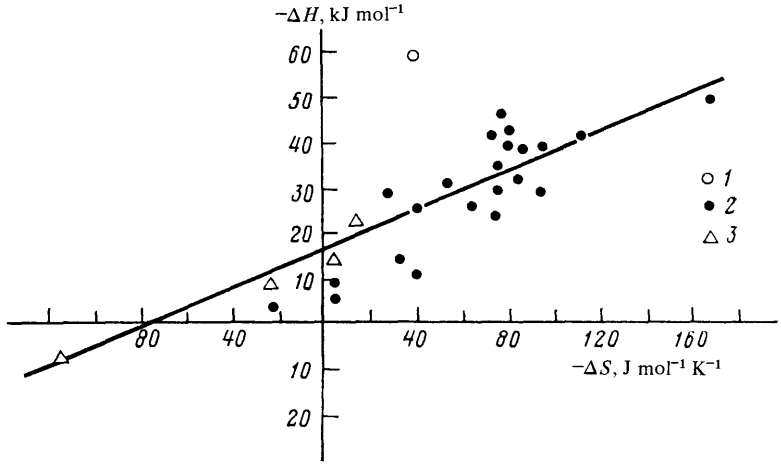


Figure 3. The isoequilibrium relation for exciplexes: *1*) singlet exciplexes in the vapour phase; *2*) singlet exciplexes in liquid solutions; *3*) triplet exciplexes; all the available thermodynamic literature data were used to plot the figure; the ΔH and ΔS for the triplet exciplexes were taken from Refs.60, 63, and 81.

3. Triplet Exciplexes of Carbonyl Compounds

The molecules of carbonyl compounds (quinones, ketones, aldehydes, and others) as a rule undergo photochemical reactions after transition to the triplet state.[67] Depending on the characteristics of their chemical structure, the lowest triplet state of carbonyl compounds can be $\pi\pi^*$, $n\pi^*$ or one of a mixed type. The most important photochemical reactions of organic compounds of this class are in one way or another related[68] to electron transfer, i.e.

$$\left(\rangle C{=}O\right)^* + D \rightarrow \left(\rangle C{=}O\right)^{\cdot-} + D^{\cdot+}$$

or the transfer of a hydrogen atom, i.e.

$$\left(\rangle C{=}O\right)^* + RH \rightarrow \rangle C^{\cdot}{-}OH + R^{\cdot}.$$

In those cases where the reactant RH molecule can serve as both an electron and hydrogen donor, the mechanism of the chemical reactions of the carbonyl compounds occurring under the influence of light is determined by the electronic structure of the excited state.[69]

In the early studies devoted to the photochemical reactions of carbonyl compounds, it was already suggested that these reactions proceed with participation of intermediate excited complexes.[70] However, until the end of the 1970's there were no experimental data of any kind confirming this view. It was first justified experimentally in a study[71] of the quenching of the phosphorescence of benzil PhCOCOPh by anisole and benzonitrile in liquid solutions. In these systems, the quenching of the phosphorescence was exponential, but the dependence of the quenching rate constants on the quenching agent concentration was non-linear. As in the quenching of the triplet molecules of porphyrins, these kinetics are determined by the formation of triplet exciplexes with a lifetime shorter than that of the triplet benzil molecules. The stability constants of these complexes are low (0.12–0.13 litre mol^{-1}).

The quenching of the triplet benzil molecules by triethylamine in moist acetonitrile has been investigated[72] using the method of laser photolysis. The bands of the benzil radical-anions were observed in the variable absorption spectrum. The rate of accumulation of this product proved lower than the rate of deactivation of the triplet molecules of the carbonyl compound, which provided the authors with justification to claim[72] that the electron phototransfer products are formed as a result of the dissociation of a highly polar relatively long-lived triplet exciplex.

The spectrum of the triplet exciplex of the carbonyl compound was first described in communications[74,75] reporting the results of the investigation of the quenching of triplet 2,6-diphenyl-1,4-benzoquinone molecules by tertiary amines. Excited molecular complexes of this type were examined in detail in a recently published review[73] and for this reason they will be only briefly characterised in the present communication.

The excited EDA compounds of ketones and quines can be both highly polar[74–78] and local excited.[78,79] the contribution of the wave function of the ionic state to the molecular wave function of the triplet exciplex is determined by the donor–acceptor properties of the reactant molecules. This question has been investigated in detail in relation to the triplet exciplexes of various quinones and aromatic electron donors.[73] In conformity with the treatment in the introductory Section, in those cases where the energy of the charge-transfer state is greater than or close to the energy of the triplet state of the quinone, locally excited complexes are formed. Their absorption spectra, like those of other locally excited molecular compounds, are close to the absorption spectra of the corresponding locally excited components—in the given instance quinones. The decrease in the energy of the charge-transfer state gradually increases its contribution to the excited complex state. The absorption spectra of such exciplexes, in which the charge transfer state has a lower energy than the energy of the locally excited state, consist of a superposition of the spectra of the corresponding radical-anion and radical-cation. The charge transfer energy is determined also by the solvating properties of the medium and for this reason the addition of even relatively small amounts of methanol (approximately 5%) leads to spectral changes indicating a marked increase in the polarity of the intermediate species.[78] An analogous phenomenon occurs also for triplet exciplexes of porphyrins with electron acceptors.[48]

The nature of the quenching agent determines the lifetimes of the triplet exciplexes. For complexes with the lowest locally excited state, the deactivation rate constants are close to those for the corresponding quinone molecules.[78] This feature is evidently a manifestation of the general feature, already examined, of locally excited molecular compounds. The lifetimes of highly polar triplet exciplexes of carbonyl compounds depend on the energy of the charge-transfer state: the smaller this energy, the higher the rate of deactivation.[77,78] This is apparently a manifestation of the energy gap law,[80] according to which the rate of the non-radiative transition increases with decrease in the difference between the energies of the corresponding energy levels.

A detailed kinetic analysis of the quenching of the triplet states of acetone by durene, which takes place with formation of a weakly polar triplet exciplex as an intermediate, has been carried out.[81] The rate constant for its formation is approximately two orders of magnitude smaller than the rate constant for the diffusion-controlled process. Like the locally excited complexes of porphyrin compounds, the triplet exciplex of acetone with durene has a low enthalpy of formation ($\sim$23 kJ mol^{-1}) and a less negative entropy of formation (–14 J mol^{-1} K^{-1}) than the typical singlet exciplexes. It is important that thermodynamic parameters of this triplet exciplex satisfy the thermodynamic compensation relation examined above.

4. Triplet Exciplexes of Dyes and Related Compounds

The triplet exciplexes formed by representatives of other classes of organic compounds have been much less investigated. In the literature, it is possible to find only individual scattered data concerning the triplet exciplexes of aromatic hydrocarbons, dyes, and heterocyclic compounds.

It has been reported[82] that the pulse photoexcitation of degassed toluene solutions containing *NN*-dimethylaniline apart from a phenazine compound leads to the apperance of a relatively long-lived variable absorption signal, whose spectrum differs from that of the triplet–triplet absorption spectrum of the initial phenazine compound. The authors[82] suggested that the observed intermediate species are triplet exciplexes. Data indicating complex quenching kinetics have been confirmed in a communication[83] where it was reported that the quenching of the long-lived component of the kinetic curve is non-exponential and, furthermore, that these signals are observed in oxygen-saturated solutions. However, later careful studies demonstrated[84] that the intermediates produced on quenching the triplet molecules of phenazine compounds by amines are nevertheless deactivated by oxygen with rate constants which do not differ greatly from the rate constants for diffusion-controlled processes. These intermediates are most probably triplet exciplexes.

Triplet exciplexes are evidently formed also on pulse photoexcitation of the 9-phenylacridinium cation in the presence of organic electron donors in liquid solutions.[85] These exciplexes have an unusual electronic structure: they represent, as it were, the complexes of the uncharged 9-phenylacridine radical and the radical-cation of the corresponding electron donor. Such triplet exciplexes are extremely stable even in polar media. The corresponding equilibrium complex formation constants are approximately 10^5 litre mol^{-1}. Such high stability of the triplet 9-phenylacridinium exciplexes also apparently cannot be accounted for by energy factors, because there is virtually no Coulombic interaction between the components in these excited molecular compounds. Their characteristic feature is that they are formed as a result of the intersystem crossing in the corresponding singlet exciplex, since the quantum yield of the triplet state of the 9-phenyl-acridinium cation is extremely low. This mechanism of the formation of the triplet states of molecular complexes will be examined in the next Section.

Usacheva et al.[96] investigated the intermediates formed on quenching the triplet state of eosin by an electron acceptor (methylviologen) in water. It was found that the quenching is accompanied by the formation of a short-lived intermediate whose absorption spectrum differs appreciably from that of the triplet eosin molecules. At the same time, it was shown that "free" radical species are not formed in the given system. On this basis, one can conclude that the observed intermediate is a triplet exciplex with a significant contribution by the charge-transfer state.

The question of the formation of triplet exciplexes on quenching of the triplet states of aromatic hydrocarbons by electron acceptors is controversial. The formation of triplet exciplexes of anthracene with organic nitro- and halogeno-compounds in benzene has been reported,[40] but this result could not be reproduced by other workers.[87] The latter were unable to detect the formation of triplet exciplexes even on quenching of the triplet 1,2-benzopyrene and 1,2-benzanthracene molecules by electron acceptors. Apparently, if the triplet exciplexes are in fact formed in these systems, they have extremely short lifetimes. The difficulty of studying the products of the pulse photoexcitation of aromatic hydrocarbons is due to the factor that electron acceptors also quench effectively the singlet-excited states, reducing the quantum yield of the triplet molecules and lowering thereby the intensity of the variable absorption signals.

IV. FORMATION OF THE TRIPLET STATES OF MOLECULAR COMPLEXES AS A RESULT OF INTERSYSTEM CROSSING

The triplet states of both EDA complexes and exciplexes can be formed as a result of the intersystem reactions of singlet-excited states on radical-ion pairs. The mechanisms of these processes will be considered in the present Section.

1. Intersystem Crossing in Excited EDA Complexes

On the basis of the study of molecular complexes by nanosecond laser photolysis, it has been concluded[88,89] that in frozen solutions an appreciable if not the main fraction of the triplet states of molecular complexes are produced during the laser flash as a result of intersystem transitions from the unrelaxed Franck–Condon singlet-excited state. Almost simultaneously, an analogous mechanism was put forward also for the intersystem crossing in exciplexes.[90] However, subsequent studies carried out using picosecond laser spectroscopy[91] disproved this mechanism. Although CTC have not been investigated by this method, nevertheless one can postulate that, in donor–acceptor compounds which are stable in the electronic ground state, the intersystem period in liquid solutions should involve mainly the classical mechanism i.e. the relevant transition should be from the thermalised fluorescent state. In frozen solutions the intersystem crossing can take place from the Franck–Condon state, because the structural rearrangements of the complexes in frozen solutions are greatly hindered and the Franck–Condon state is fluorescent.[92,93]

The rates and hence the yields of the intersystem crossing depend on the degree of charge transfer between the components of the complex in the triplet state. The following selection rules have been formulated[94] for the intersystem crossing in EDA complexes: the non-radiative transition between the singlet and triplet charge-transfer states must take place at low rates in contrast to the intersystem transitions from singlet charge-transfer states to the triplet states with a locally excited nature. These postulates were based on the fact that the matrix elements of the spin–orbit coupling of the singlet and triplet charge-transfer states are zero,

$$\langle {}^1\psi(A^-D^+)\,|H_{co}|\,{}^3\psi(A^-D^+)\rangle = 0\ , \qquad (18)$$

in contrast to the matrix elements of the spin–orbital coupling of the singlet-excited charge-transfer states and triplet locally excited states:

$$\langle {}^1\psi(A^-D^+)\,|H_{co}|\,{}^3\psi(D^*A)\rangle = -\langle \pi_a|H_{co}|\pi_d\rangle\ . \qquad (19)$$

In Eqns.(18) and (19), π_a is the highest unoccupied orbital of the acceptor, π_d the highest occupied orbital of the donor, and H_{SO} the Hamiltonian of the spin–orbital coupling. The selection rules formulated by Lim et al.[94] agree with the qualitative estimation of the role of the non-radiative transitions

$$S_1 \rightsquigarrow T \text{ and } S_1 \rightsquigarrow S_0$$

in the deactivation of singlet-excited states of various molecular complexes.[94] The main pathway to the deactivation of singlet-excited states of the CTC of tetracyanoethylene with benzene and its alkyl derivatives, whose triplet states are charge-transfer states, is internal conversion. The lowest triplet states of the complexes of the same donors with tetracyanobenzene are of the locally excited type. In conformity with the selection rules formulated, the rate of interconversion for such molecular compounds exceeds the rate of the internal degradation of the electronic excitation energy of the EDA complex. We may note that the conclusions by Lim et al.[94] concerning the pathways followed in the transformation of the electronic excitation energy were made on the basis of indirect data concerning the influence of the deuteriation of the electron donor molecules on the fluorescence quantum yields of the molecular complexes. The introduction of deuterium into the methyl group induces the strongest effects, because their C–H vibrations have the role of promoting modes in internal conversion proceses. For intersystem transitions between close-lying states, the high-frequency C–H vibrations do not fulfil this role. The influence of their isotope substitution on the rates of the transitions

$$S_1 \rightsquigarrow T$$

should therefore be small. the study of the usual and deuteriated complexes makes it possible to determine which of the non-radiative processes—non-radiative degradation or intersystem crossing—deactivates the singlet-excited CTC states. The conclusions reached

from the analysis of the isotope effects are confirmed by phosphorescence measurements, as shown by the analysis of Nagakura's data.[2]

2. Intersystem Crossing Processes Involving Exciplexes

The photoexcitation of solutions of fluorophors containing quenching agent concentrations for which only the bands of exciplexes are observed in the fluorescence spectrum is accompanied by the appearance of relatively intense absorption bands of the triplet molecules of one of the components of the exciplex. In many cases, the calculated interconversion yields proved to be the same or even higher than in the solutions of the same fluorophors without specially introduced quenching agents.[95] It is important that these effects were observed in systems where there were no heavy atoms intensifying the spin–orbit coupling and accelerating the intersystem transitions.

The triplet–triplet absorption bands under discussion are apparently due to the "free" triplet molecules or locally excited triplet exciplexes. It is usually assumed that the primary products of the intersystem transformations of singlet exciplexes are triplet-excited complexes, but the latter are unstable owing to the low enthalpies of formation and decompose immediately (see, for example, Goldschmidt et al.[95]). This postulate, which has become generally accepted, requires an experimental test in each individual case. This is indicated by the data, discussed above, demonstrating the high stability of the locally excited triplet exciplexes of porphyrin compounds, acetone, quinones, and the 9-phenylacridinium cation, which cannot have high enthalpies of formation. Furthermore, relatively stable triplet exciplexes are formed by phenazine compounds with tertiary amines.[82,84] Singlet fluorescent exciplexes, which may undergo intersystem crossing, are also observed in these systems.[96]

However, despite some uncertainty in the question of the form—"free" or as part of a complex—in which the excited triplet molecule exists, the triplet–triplet absorption recorded in exciplex systems indicates relatively high intersystem crossing yields of the singlet-excited exciplexes.

Studies carried out by the laser photolysis methods have shown that the intersystem crossing in exciplexes takes place after the formation of thermalised fluorescent states. For example, it has been established[97–99] that, as the variable absorption of the exciplex of *NNNN*-tetramethyl-*p*-phenylene-diamine with naphthalene and biphenyl and of anthracene with *NN*-dimethylaniline is quenched, an increase in the intensity of the triplet–triplet absorption band is observed. The kinetics of the accumulation of the triplet molecules then also correspond to the kinetics of the relaxation of the optical density of the absorption band of the singlet-excited complexes. Agreement between the rates of these processes has also been noted in a study[100] of exciplexes of anthracene and pyrene with *NN*-diethylaniline in hexane using the picosecond technique. During the first 200 ps after the laser flash, there were no bands due to triplet molecules in the variable absorption spectrum. This period was sufficient for virtually all the excited species to enter into complex formation and for the excited complexes to pass to the thermalised state. After long periods, an increase in the triplet–triplet absorption, accompanying the destruction of the exciplexes, was observed. These results demonstrated that in non-polar media the intersystem crossing and the fluorescence of the exciplexes are consecutive and not parallel processes.

The formation of triplet states from relaxed exciplexes takes place also in complexes formed as a result of the conformational changes in photoexcited bichromophoric $A-(CH_2)_n-D$ molecules, in which the donor and acceptor groups are linked by a flexible aliphatic chain.[101]

Thus it can now be regarded as established that in non-polar solvents the triplet states are formed as a result of intersystem transitions from relaxed charge-transfer states of the molecular complexes. On this basis, the rate of the intersystem crossing in the exciplex k_T' can be calculated from the formula[102]

$$\frac{k_T'}{k_T} = \frac{(\varphi_T/\varphi_T^0)(\varphi^0/\varphi) - 1}{(\varphi^0/\varphi) - 1} \cdot \frac{\tau_0}{\tau_0'},$$

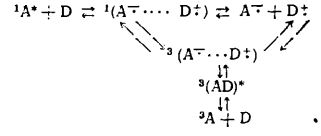
where τ_0 is the lifetime of the excited fluorophor in the absence of quenching agents, τ_0' the lifetime of the exciplex, φ^0 and φ are the fluorescence quantum yields, and φ_T^0 and φ_T are the quantum yields of the triplet molecules in the absence and presence of the quenching agent respectively.

The rate constants and quantum yields of the intersystem crossing in exciplexes are determined by the nature of the reactants. For example, quenching of the fluorescence of pyrene and anthracene by amines increases the yield of the triplet state of the hydrocarbons.[95] The formation of exciplexes of *NN*-dimethyl-β-naphthylamine with dimethyl isophthalate lowers the yields of the triplet molecules compared with the yield of the triplet molecules of the above amine in the absence of a quenching agent.[103] We may quote yet another example. The rate constants for the intersystem crossing in the exciplexes of 9,10-dicyanoanthracene with aromatic hydrocarbons are approximately 10^7 s^{-1} and those for the exciplexes with tertiary amines are approximately 10^9 s^{-1}.[102] Many of the features of the intersystem crossing in exciplexes can apparently be explained using the selection rules formulated in the previous Section, according to which the intersystem transitions in molecular complexes take place between charge-transfer and locally excited triplet states. The quantum yields in the formation of the triplet molecules diminish as a result of complex formation if the triplet locally excited states have a higher energy than the fluorescent state of the exciplexes. Another factor influencing the yield of the triplet molecules can be a change in the structure of the exciplex. This postulate has been confirmed by the results of a study on the intersystem transitions in intramolecular exciplexes.

The structures of the intramolecular exciplexes are known to be determined by the length of the chain linking the electron donor and electron acceptor groups.[104] For $n = 3$, there is a possibility of the formation of sandwich structures with a parallel arrangement of the planes of the donor and acceptor components. In such exciplexes, the intersystem transitions take place at relatively low rates close to the rates of the intersystem transitions in the majority of aromatic molecules (approximately 10^7 s^{-1}).[101] For $n = 1$ or 2 in singlet exciplexes, the molecules are arranged in planes which are almost perpendicular with respect to one another.[105] The transition from the sandwich to the "perpendicular" structure induces a marked increase in the rate of intersystem crossing.[101] These changes are explained by an increase in the matrix elements of the spin–orbit coupling of the corresponding states, whose values determine the rates of the intersystem transition. The rate of intersystem crossing can evidently be influenced, apart from the factors indicated, also by the charge distribution in the complexes and by the distance between the donor and acceptor groups. As a consequence of this, the rates of the intersystem transitions in exciplexes are extremely sensitive to

various structural factors. It is therefore not surprising that solvents capable of influencing appreciably the structures of excited molecular complexes alter the rates of the transitions from the single-excited to the triplet-excited states. As an example, one may quote again intramolecular exciplexes. An increase in solvent polarity weakens the Coulombic attraction of the charged parts of the exciplex. This alters the structure of the excited complex, which is reflected in the absorption spectra of the exciplexes.[106] Pronounced solvation induces conformational transitions and alters thereby the spin–orbital coupling and the rate of intersystem processes.[101] However, in the study of the influence of the solvent on the spin evolution of the intermolecular exciplex systems, it is essential to take into account the fact that in highly polar media there is a possibility of the operation of completely different mechanisms of intersystem crossing. In this connection, we shall characterise briefly the mechanisms of the formation of triplet-excited molecules in polar media.

In polar solvents, the quenching agent interacting with a singlet-excited molecule can also induce its transition to the triplet state. For example, the flash photoexcitation of acetonitrile solutions of aromatic hydrocarbons and electron donors (or acceptors) induces the appearance of triplet hydrocarbon molecules apart from the radical-ion products.[95] The mechanism of these photoprocesses has been established with the aid of nanosecond and picosecond laser photolysis.[107,108] In highly polar solvents, triplet states are formed as a result of at least two main types of reactions—the relatively slow recombination of the free radical-ions and the rapid intersystem crossing in the geminal radical-ion pairs. It is quite possible that the primary products of the geminal recombination of the radical-ion pairs are triplet exciplexes:[109,110]



It has been suggested that the intersystem transition from a singlet radical-ion pair to a triplet pair takes place via the so called hyperfine interaction mechanism, which is indicated by data concerning the influence of weak magnetic fields on the yields of triplet states.[101]

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The Study of the Boundary Viscosity of Organic Liquids by the Blow-off Method

B.V.Deryagin and V.V.Karasev (deceased)

A method is described for the investigation of the boundary viscosity of liquids based on the fact that, when a layer of liquid flows on a flat wall under the influence of a stream of gas flowing above it, the film assumes a wedge-shaped form (the blow-off method). It is shown that the profile of the resulting wedge resembles that of the velocity profile, which makes it possible to determine from this profile the viscosity as a function of the distance to the support. Another method for the layer-by-layer determination of the viscosity is based on the measurement of the thickness of the film as a function of the duration of the blow-off process at a specific distance from the wetting boundary. In order to determine the film profile, optical and especially ellipsometric methods have been used.
In order to extend the range of objects of study, a method has been developed for the investigation of the boundary viscosity of volatile liquids and its theory has been specified. It has been applied to hexadecane and it has been observed that the viscosity decreases at short distances from the wall.
The bibliography includes 67 references.

CONTENTS

I. Introduction 634
II. The blow-off method 635
III. Apparatus for the study of the boundary viscosity by the blow-off method 635
IV. The study of the boundary viscosity of liquids by optical methods 637
V. The study of the boundary viscosity of organic liquids in the blow-off process 643
VI. The study of the boundary viscosity of volatile liquids 645

I. INTRODUCTION

The theory of the stability of colloids[1] is based on the idea of the wedging pressure of thin liquid layers and its components. In devising a theory of lyophobic disperse systems, only two components of the wedging pressure were initially taken into account – the ionic-electrostatic and molecular components.[1] Subsequently, the concept of the structural component of the wedging pressure, for brevity referred to as the structural forces, was introduced to account for the stability of lyophilic disperse systems. The idea of the existence of this component was first put forward by one of the authors of this review on the basis of experiments with wetting and absorption layers on hydrophilic surfaces.[2-5] These forces arise as a result of the overlap of the boundary layers, whose structure has been made anisotropic in contrast to the isotropic structure of the same phase in bulk. On this basis, attempts have been made to create a quantitative theory of structural forces.[6,7]

In order to strengthen the very basis of this approach, it is important to establish by independent, direct methods the existence and to elucidate the character of the structural features of the boundary layers on lyophilic supports. The difficulty of this problem is due to the small thickness and the possible inhomogeneity of boundary layers with an unusual structure. Dielectric structural methods therefore usually yield only an average characteristic. An exception is the method based on the determination of the weakening of the plane-polarised light transmitted through a thin layer of liquid as a function of the thickness of the latter, which has been proposed and developed by Popovskii, Altoiz, and other workers.[8-18] However, this method is applicable only to a specific class of liquids, for example, to substituted benzenes or benzoic acids, which exhibit a specific strong absorption in a definite part of the spectrum.

This review describes the outcome of experiments on the "layer-by-layer" measurement of viscosity by the method involving the blowing off of wetting films of various organic liquids. These measurements made it possible to establish the changes in viscosity occurring as the solid support is approached, as a function of the distance from it. The change in the structure of the liquids in layers near the support under the influence of the latter has been demonstrated thereby, since viscosity is a property sensitive to structural characteristics.

The determination of the viscosity of thin liquid layers is of direct interest for the study of the mass-transfer processes in narrow capillaries, slits, and disperse systems, in particular for the treatment of the boundary lubrication and filtration phenomena and membrane processes.

The flow of liquid through narrow capillaries was used in early investigations, for example in those of Traube and Siar-Hong-Wang[19] and Deryagin and Krylov,[20] who observed anomalous phenomena in the flow of water in porous bodies with a pore diameter of 0.15 μm. It was also found that, as a result of the coating of the pore walls by oleic acid monolayers, the flow rate increased by a factor of 7 (see also the studies of Somov and Churaev[21] and Peschel and Adlfinger[22]).

Deryagin and Samygin developed a centrifugation method.[23,24] It is based on the observation of the movement of a cylindrical air bubble in a sealed tube filled with the test liquid. The movement of the bubble in the direction of the centrifuge axis takes place as a result of the flow of liquid, forming a film between the air bubble and the walls of the tube, in the opposite direction. The viscosity η was calculated from the formula

$$\eta = \frac{2}{3}\frac{h^3}{rv} j \quad ,$$

where r is the radius of the tube, v the velocity of the bubble, j the centripetal acceleration, and h the thickness of the film.

In order to determine the film thickness h, the ends of the tube were narrowed. We shall denote by V_1 and V_2 the volumes of the liquid in these capillary ends by S the area of the film. By vigorous centrifugation with simultaneous heating, the liquid and the wetting film were driven to one end of the tube in which they occupied a volume V_0. The film thickness was determined from the formula

$$h=\frac{V_0-V_1-V_2}{S} .$$

An increase in viscosity at a distance of 0.1 μm from the wall was observed for certain liquids by this method. In one case it was possible to estimate the increase in viscosity at a distance of 0.02 μm. Hence it is clear that the centrifugation method is more sensitive than all previous procedures. However, in this method too the flow of liquid takes place under the influence of volume forces, which precludes the determination of the viscosity as a function of the distance from the wall.

II. THE BLOW-OFF METHOD

The layer-by-layer method for the measurement of the boundary viscosity—the blow-off method—proposed by one of the authors of the present review,[25,27] is a unique procedure which makes it possible to determine the distribution of the viscosity along the thickness of the boundary layer by the most direct and clearest procedure. Its essential feature is as follows. Imagine a channel bounded by two parallel planes which are separated from one another by a small distance $H = 0.2-1.0$ mm; a layer of the test liquid is deposited on one of the walls (Fig.1). When air or nitrogen is blown through, a flow arises in the film. The drop in air pressure arising between the ends of the channel is measured with a differential manometer.

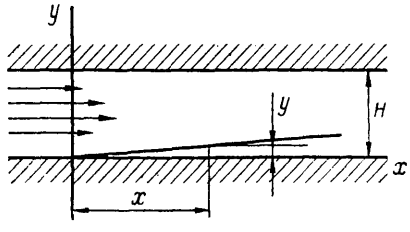


Figure 1. Schematic illustration of the blow-off method.

Tangential and normal forces act on the film. It has been shown that, when a number of conditions are satisfied, the gradient of normal forces may be neglected; in other words, the inequality

$$\delta=\frac{Q_2}{Q_1}\ll 1 ,$$

where Q_1 is the flux under the influence of tangential forces and Q_2 the flux under the influence of the gradient of normal forces, is valid.

If the law of conservation of momentum is applied to the mass of air moving in a slit, we have

$$H\Delta p-2\bar{F}\Delta l=\Delta\int_0^H \rho v^2\,dy ,$$

where $\bar{F}$ is the average tangential frictional force, Δl the length of the slit, ρ the density of air, v the velocity of air molecules, H the slit width, and Δp the pressure difference between the two ends of the slit. Taking into account the continuity equation and applying the parabolic law of the distribution of velocity in a slit, we obtain after appropriate transformations

$$H\Delta p=2\bar{F}\Delta l+\frac{8}{15}H\rho v\Delta v . \qquad (1)$$

Using the relations

$$F=\left(\frac{\partial v}{\partial y}\right)_{y=0}=4\eta\frac{v}{H} ,$$

$$\mathrm{Re}=H\rho v_{max}/\eta ,$$

where η is the viscosity, Re the Reynolds number, and v_{max} the maximum velocity at the centre of the slit, we finally obtain after substitution in Eqn.(1)

$$\frac{\Delta p}{\Delta l}\cong\frac{dp}{dl}=\frac{2\bar{F}}{H}+\frac{2}{15}\mathrm{Re}\frac{\Delta F}{\Delta l} . \qquad (2)$$

On substituting the resulting expression in the formula for the flux ratio, we have

$$\frac{Q_2}{Q_1}=\frac{4}{3}\frac{h}{H}+\frac{4}{15}\mathrm{Re}\frac{h}{\Delta l}\frac{\Delta F}{\bar{F}} . \qquad (3)$$

In order that δ should be small, the ratios h/H, $h/\Delta l$, and $\Delta F/\bar{F}$ should be small. As regards the first condition, it is permissible that $h/H \leqslant 0.01$. The inadmissability of the variation of $\bar{F}$ along the air stream requires that the inequality $\Delta F/\bar{F} < 0.05$ should hold, which was always the case in our measurements. Applying the continuity equation and the Boyle–Marriotte law, we replace $\Delta F/\bar{F}$ by $\Delta p/p$ and obtain the condition $\Delta p/p < 0.05$, which can be readily achieved at $p = 760$ mmHg; $h/\Delta l$ was always less than 10^{-4} in our experiments.

It it is assumed that $\mathrm{Re} < 10^3$, which corresponds to the condition for a laminar blowing off stream, then we obtain $\delta < 1.4\times 10^{-2}$ from Eqn.(1). Assuming simultaneously that $\Delta F/F < 0.05$ and $H/\Delta l < 0.005$, we find from Eqn.(2) that the following relation is valid with a relative error of approximately 2%:

$$\bar{F}=\frac{H}{2}\frac{\Delta p}{\Delta l} .$$

For sufficiently small values of δ, the flow of the film solely under the influence of tangential forces is ensured. By virtue of this condition, the velocity of the molecules is a function solely of the distance from the wall y and is independent of the distance x from the wetting boundary—a situation resembling the collapse of a pack of cards. In particular, the points located on the outer surface of the wetting film also have the same velocity $u(y)$. The velocity of the latter can be found from the change in the film profile obtained as a result of the blow-off process. If the initial profile is described by the expression $x = x_0(y)$ and the final profile, after a time τ has elapsed, is described by the expression $x = x(y)$, then $x = x_0 + u(y)\tau$. One can then write $u(y) = [x(y) - x_0]/\tau$. The viscosity can be inferred from the profile:

$$\eta(y)=\frac{F}{du/dy} .$$

When η is constant, the quantity du/dy must also be constant, which corresponds to the equation $x(y) = \text{const.} \times y$, i.e. the film assumes the form of a wedge with a flat surface. The increase in η for low volumes of y leads to the "blunting" and its decrease to the "sharpening" of the wedge.

III. APPARATUS FOR THE STUDY OF THE BOUNDARY VISCOSITY BY THE BLOW-OFF METHOD

The apparatus for the study of the boundary viscosity by the blow-off method,[28,29] illustrated in Fig.2, consists of a metallic block *1* with a groove, open on top, having a semicircular cross-section, to which two smaller blocks *2* with tubes *7* and channels for the admission and release of gas are attached. Flexible tubing, connecting the

apparatus to the source of gas (nitrogen cylinder, air blower, etc.), is attached to one of the tubes *7*. In block *1*, there is a groove in which a steel insert *3* is placed. A steel or glass plate *4* with an optically polished lower surface is put on top of the apparatus. A gap is formed between the plate *4* and the insert *3* through which air or nitrogen is blown. By selecting the size of the inserts, it was found that the most suitable gap is 0.2 mm. In order to determine the pressure drop in the block *1*, two channels *5* were drilled and connected to the tubes *6*, to which a differential manometer was also connected. The film of the test liquid is deposited on part of the upper plate *4* or on part of the insert *3*. The wetting boundary must be located at right angles to the direction of the stream of gas (Fig.2, line *aa*). A steel plate from the "Kalibr" factory with additional optical polishing was used as the support.

The surface was cleaned with ether. In those cases where special cleanliness was required, the cleaning was carried out with the aid of a gas discharge in argon.[30] The film was deposited by the draining method developed by one of the authors of the present review.[31-33] Several drops of the test liquid were placed on the surface of the plate and the wetting boundary was smoothed out with a thin glass rod. In this deposition method, the film has an inhomogeneous thickness in the initial instant. However, special experiments showed that, in conformity with the theory, this is in no way reflected in the pattern obtained in the blow-off process even after a short time. An apparatus for the study of the boundary viscosity with a variable gap has also been used.[34]

In those cases where special cleanliness is required (for example, in the study of solutions of organic compounds at a low concentration in liquid paraffin) a glass device capable of being disassembled was used,[29] its components being washed with chromic acid mixture, which was followed by treatment in the gas discharge.

Turbine oil and solutions of "metallic soaps" in turbine oil, which are used to improve the lubricating properties of liquids, were investigated for the first time by the blow-off method.[25,26]

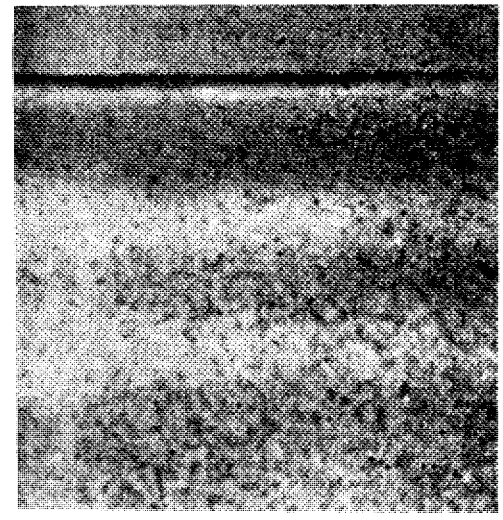


Figure 3. Interference pattern obtained in an experiment involving the blowing off of a 2% solution of aluminium naphthenate in turbine oil; blow-off time 8 min.

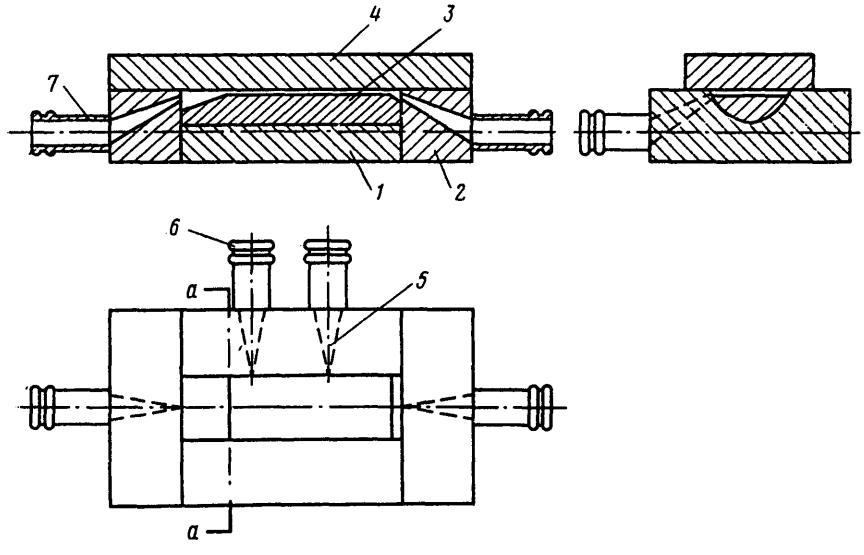


Figure 2. Apparatus for the investigation of the boundary viscosity by the blow-off method.

IV. THE STUDY OF THE BOUNDARY VISCOSITY OF LIQUIDS BY OPTICAL METHODS

1. Determination of the Thickness of Layers by the Interference Methods

Fig.3 presents the interference pattern obtained for a 2.5% solution of aluminium naphthenate in turbine oil The photograph shows the narrow first band, which indicates an increase in the viscosity of the liquid near the wall. The interpretation of this interference pattern leads to the velocity profile illustrated in Fig.4. A similar velocity profile is also observed when aluminium naphthenate is added to other oils.

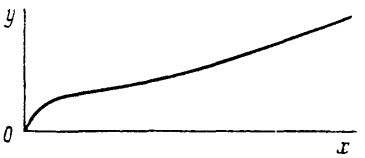


Figure 4. Velocity profile of a 1−2% solution of aluminium naphthenate.

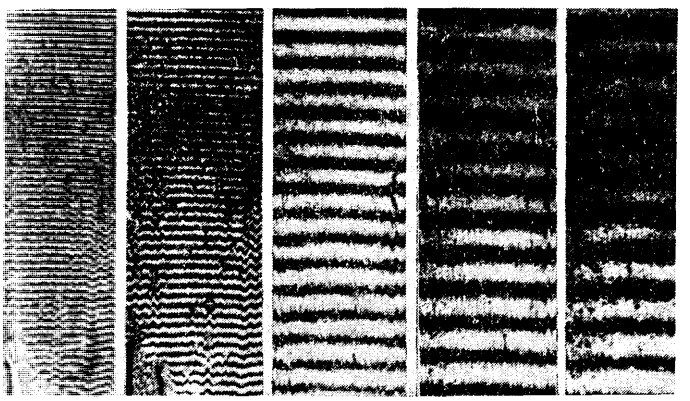


Figure 5. Inteference pattern obtained during the blowing off of turbine oil.

A series of studies have been carried out [35,36] on the properties of various high-molecular-weight organic liquids and solutions of certain polymers in turbine oil and liquid paraffin. For convenience, the authors recorded the blow-off process by filming it. The thickness of the wedge-shaped film was determined from the formula $h = (2n + 1)\lambda/4$, where n is the number of the interference band and λ the wavelength of the monochromatic light. Turbine oil was tested initially. It is seen from the film frames shown in Fig.5 that the distances between the bands are identical. Consequently the viscosity is independent of the distance from the supports, which agrees with the results of earlier studies.[25,26] The pattern is quite striking. The movement of the bands apart as a function of time is observed with a gradual retardation. The thin bands located approximately at right angles to the interference bands represent a parasitic phenomenon due to the interference in the blow-off channel by virtue of the very highly monochromatic nature of the light source.

Fig.6 presents film frames which illustrate the flow of hexamethoxydecane, having an increased viscosity at the boundary with the metal. In this case a small increase in viscosity within the limits of two to three bands is observed. Fig.7 illustrates the flow of a layer of tetraethoxyhexane; in this case the viscosity decreases within the limits of the first two bands. In order to investigate the behaviour of polymers at different temperatures, the apparatus was thermostatted.[37]

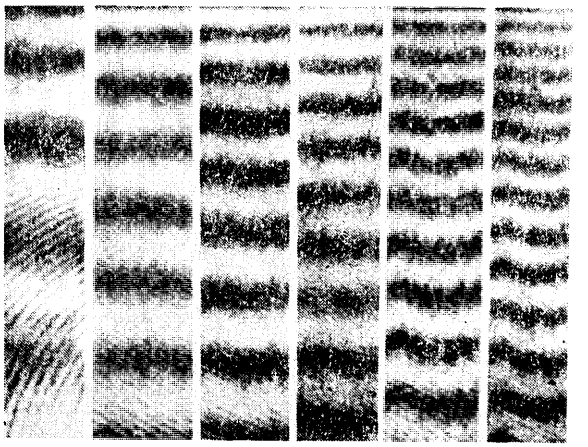


Figure 6. Interference pattern in the course of the blowing off of hexaethoxydecane.

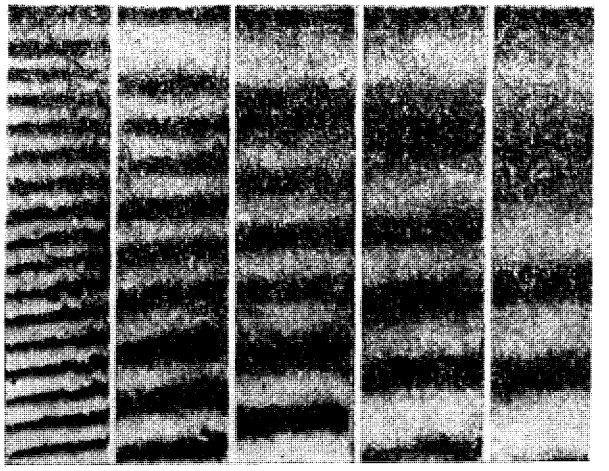


Figure 7. Interference pattern in the course of the blowing off of tetraethoxyhexane.

In the study of polymers of butyl vinyl ether (vinipol) and their solutions in turbine oil and certain other liquids, a change in viscosity was observed as a function of the distance from the solid wall within the limits of $\pm(5-6)$ μm. It was noted that, after the attainment of a definite film thickness, the interference bands disappear and a "ripple" appears on the surface of the film.[35-37] This instability extends over a distance up to 10 μm (Figs.8 and 9). The maximum instability is observed at certain added concentrations of vinipol in turbine oil, which are lower the higher the molecular weight of the vinipol.

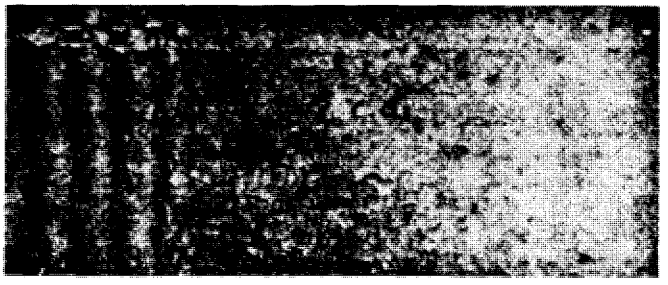


Figure 8. Interference after blowing off a 0.5% solution of vinipol with a molecular weight M = 3850 in turbine oil (Δp = 15 mmHg, τ = 5 min); the break up of the film can be seen (instability zone).

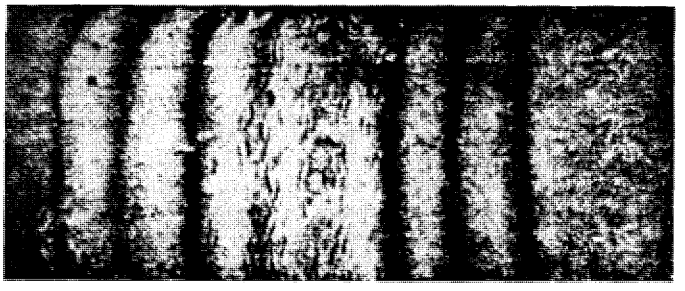


Figure 9. Interference pattern after blowing off a 0.04% solution of vinipol with M = 2100 in turbine oil (Δp = 25 mmHg, τ = 22 min).

In certain cases instability is observed also for "pure" polymers with a narrow molecular weight distribution (MWD). With increase in the molecular weight of vinipol, the thickness of the film, outside the limits of which the region of instability of the interference pattern begins, increases. The instability is manifested to a greater extent if the blowing off is preceded by prolonged contact between the film of the polymer solution and the metal. With increase in temperature, the instability of films of vinipol solutions grows very little, in contrast to the pure vinipol. It follows from thermodynamic considerations that the instability of the wetting film indicates that, in the corresponding range of thicknesses, the derivative of the wedging pressure with respect to the film thickness is positive. Since films whose thickness amounts to several micrometers are unstable, it follows that for such thicknesses the wedging pressure and its derivative have values sufficiently high for the breakdown of liquid films even when their viscosity is high. Evidently the structural component of the wedging pressure is manifested here.[38]

In order to investigate films with a smaller thickness, more accurate optical methods were employed. The photometric method was used first.[39,40] For this purpose, the outlet slit of the monochromator was projected onto the wedge shaped film obtained in the blow-off process. The film thickness was calculated from the intensity of the reflected light. A linear velocity profile was obtained by this method for carefully purified liquid paraffin, which indicates the absence of a specific boundary viscosity.

Polarimetric methods were used to increase the sensitivity still further.[28]

2. Measurement of the Film Thickness by Polarimetric Methods

The scheme illustrated in Fig.10 was used when polarimetric methods were applied to the measurement of the film thickness. When plane-polarised light is reflected from the plate with the film deposited on it, the components of the electric vector of the light wave, lying in the incidence plane and in the plane perpendicular to it, have different reflection coefficients, whose ratio depends on the film thickness. Knowing the ratio of the reflection coefficients, it is possible to determine the film thickness.

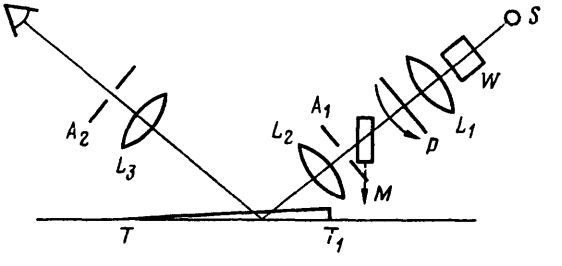


Figure 10. Schematic illustration of the apparatus for the determination of the film profile by the polarimetric method.

An apparatus with a stack of plates (Fig.10) was used to determine the ratio of the reflection coefficients. Here S is the source of monochromatic light (PRK-2 quartz lamp), W a liquid light filter (solution of neodymium nitrate with an admixture of chrysoidine and eosine), L_1 the condenser lens, P a rotating polariser (polaroid), M a stack of 9 x 12 glass plates (12 plates), A_1 an adjustable slit, L_2 a lens focussing the image of the slit onto the object, $T-T_1$ the object of study—a transparent film on a metal or dielectric, A_2 the aperture (slit) diaphragm, and L_3 an image diffusing lens.

The principle of the operation of the apparatus is as follows. If a beam of plane-polarised light is directed onto the surface of the metal with the film deposited on it, then the horizontal and vertical components of the electric vector of the light wave are in general reflected unequally, as a result of which the light flux is modulated on rotation of the polariser. The maximum intensity of the reflected light is attained when the plane of the vibrations in the rotating

polariser coincides with the direction of the most intense component of the above vector and the minimum intensity occurs correspondingly after coincidence with the least intense component (i.e. on rotation by 90°). The degree of polarisation of light transmitted through the stack of plates is known to depend on the angle between the normal to the stack and the beam incident on it. With increase in this angle as a consequence of the rotation of the stack about the axis perpendicular to the direction of the beam and parallel to the direction of the vibrations with the least amplitude, the degree of polarisation increases. Thus, we can always "attenuate" the more intense component of the electric field vector by rotating the stack, making it comparable to the least intense component. In this case modulation ceases, which is observed from the absence of periodic variations in the brightness of the reflected light. The corresponding angle of rotation of the stack depends on the ratio of the reflection coefficients of the horizontal and vertical components of the electric field vector of the light wave.

In order to increase further the accuracy of the reading and to expand the range of the measurable thicknesses towards lower values, a scheme resembling that of the Drude scheme with a photoelectric indicator was used; the scheme was applied in different versions, the locations of the light source and the indicator being interchanged.[41–46] At the present time the film thickness is calculated on a computer by means of appropriate programs.

Polished metallic surfaces are known to possess a microhardness, i.e. there are grooves approximately 40–80 Å deep and 80–160 Å wide in the direction along the plane.† At the end of the experiment, they are filled with the test liquid. However, the optical constants of the plate, measured before and after the experiment, proved to be very similar, which suggests that the liquid in the groove does not exert any special influence on the optical constants of the support. Although a random mosaic structure, consisting of islands and hollows with "diffuse" edges, filled with liquid, is observed on the surface of the metallic plate, the effective refractive index of this system remains close to the refractive index obtained for the specimen of the pure metal with a thin oxide film. Consequently, the film thicknesses are read from a certain arbitrary boundary passing near the tops of the peaks of the surface relief.

3. The Study of Certain Organic Substances by the Blow-off Method Using Polarimetric Procedures

The objects of the study of the boundary viscosity by polarimetric methods were turbine oil and liquid paraffins of different brands: paraffin purified by the acid–alkaline method, paraffin treated over a platinum catalyst by the Elovich method, D-1 oil, and pharmaceutical liquid paraffin purified chromatographically. Rigorously linear velocity profiles were obtained in all cases. After this, a 2.5% solution of vinipol ($M \simeq 4000$) in turbine oil was tested.[48] A decrease in viscosity near the wall over distances up to 1000 Å was observed in this case (Fig.11). In the study of the 0.5% solution of synthetic sodium-butadiene rubber in turbine oil,[48] some increase in viscosity in a layer 100–200 Å thick was observed (Fig.12).

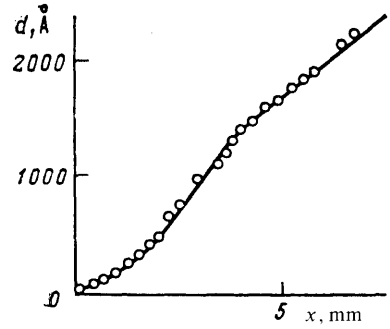


Figure 11. Film profile for a 2.5% solution of vinipol with $M \simeq 4000$ in turbine oil, obtained on the apparatus with a stack of plates.

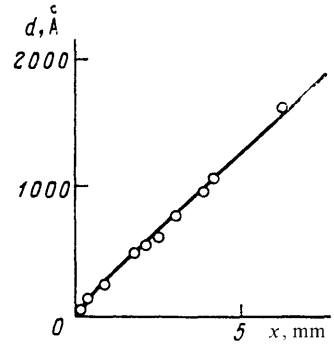


Figure 12. Film profile for a 0.5% solution of sodium-butadiene rubber in turbine oil, obtained on the apparatus with a coherence eliminating device.

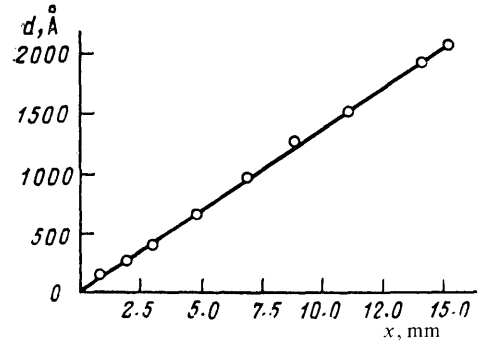


Figure 13. Film profile for purified liquid paraffin.

Further measurements were performed on ellipsometers. In the first place, the velocity profile was obtained for liquid paraffin specially purified on a platinum catalyst. The linear velocity profile was retained down to the thickness of 10 Å (Fig.13). Finally, a large number of organosilicon compounds were investigated.[49,56]

†According to electron microscope data obtained by A.E.Chalykh and Z.E.Sheshenina.

The study of the viscosity of boundary layers of polymers is of special interest from the standpoint of the elucidation of the influence of their molecular characteristics—the molecular weight, the rigidity of the molecular chain, the chemical composiiton, and the level of intermolecular interaction—on the properties of the boundary layers of polymers. We may note that organosilicon polymers and oligomers are very interesting objects for the study of the boundary viscosity. Firstly, polyorganosiloxanes retain their liquid state over a very wide range of molecular weights. Secondly, the replacement of methyl groups in polydimethylsiloxanes by other groups makes it possible to vary within fairly wide limits both the flexibility of the polymer chains of the molecule and the character and level of the intermolecular interaction in polyorganosiloxanes.[57,58]

We investigated polydimethylsiloxane liquids (PMS) with molecular weights ranging from 1000 to 40 000 and viscosities from 0.05 to 20 St[52] (at 20 °C) and a series of substituted oligo-organosiloxanes containing ethyl, phenyl, chlorophenyl, γ-trifluoropropyl, and other groups.[54] The influence of the molecular weight and of the molecular weight distribution of the polymer on its behaviour in boundary layers as well as of temperature and factors such as photo- and thermo-oxidation has been studied in relation to polydimethylsiloxanes. Their boundary viscosity was investigated on glass and metallic surfaces.

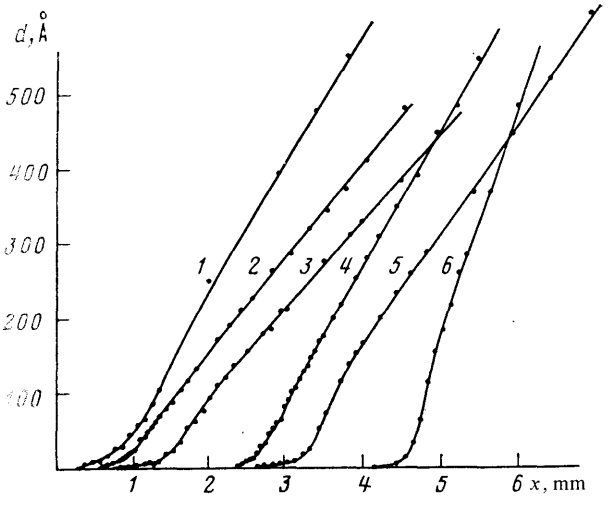


Figure 14. Film profiles for PMS having different molecular weights with a narrow MWD = 1.2–1.5 on steel: 1) PMS-5; 2) PMS-10; 3) PMS-25; 4) PMS-70; 5) PMS-400; 6) PMS-2000.

The velocity profiles for the flow of PMS films having different molecular weights and with a narrow MWD on steel are presented in Fig.14. Their common feature is the presence of three sections in the curve with different slopes and hence with different viscosities of the corresponding liquid layers. A sharp decrease in the viscosity of the liquid is observed for a layer thickness of 20–30 Å, the viscosity is 30–40% higher in the range of thicknesses from 20–30 to 150–200 Å than in the bulk phase, while the viscosity of a layer 150–200 Å thick does not differ from that in the bulk phase determined with the aid of a capillary viscometer. For example, these quantities are respectively 4.92 and 4.70 cP and 69.68 and 68.25 cP respectively for the PMS-5 and PMS-70 polydimethylsiloxanes.

Bearing in mind the extreme flexibility of the main molecular chain and the weak intermolecular interaction, the molecular structure of the PMS in the bulk phase can be represented as an assembly of species whose conformational spectrum is extremely broad—from coiled to uncoiled molecules with the former predominating. The flow velocity profile observed for PMS films can be accounted for by the variation of the conformational equilibrium of the PMS molecules in the force field of the surface of the solid phase.

The anomalously low viscosity of PMS in layers adjoining the surface of the solid phase is apparently due to the uncoiling of the molecular coils and the subsequent orientation of the uncoiled chains parallel to the plane of the support. Such orientation should be promoted by the high polarisability of the $Si^{\tau+}-O^{\tau-}$ bond, each atom of which can become a centre of attraction to the surface of the solid phase and can promote the horizontal orientation of the PMS molecules on absorption. A monomolecular PMS layer with a horizontal orientation of the molecules is known to have a thickness of 5–6 Å. Taking this into account, one can postulate that the "lower" boundary layer is made up of several horizontallly oriented layers of PMS molecules. The anomalously low viscosity can be explained in this instance by the ready slip of these layers relative to one another over planes bounded by methyl groups. The fact that the thickness of the boundary layer is independent of the molecular weight of the PMS confirms the hypothesis of the horizontal orientation of the uncoiled molecular chains. In liquid layers more remote from the support, the influence of this force field on the solid phase is weakened and the polymolecular boundary layer breaks down. The orientation of the molecules, which still have an uncoiled conformation, then becomes random; this should increase the viscosity, which has in fact been observed for liquid layers with a thickness from 20–30 to 150–200 Å. Above this level, the viscosity falls, evidently as a consequence of the coiling of the molecules, and subsequently remains constant and equal to the viscosity of the liquid in the bulk phase. In this range of thicknesses, the surface of the solid phase apparently does not influence the molecular structure of the liquid. According to the results of Fox et al.,[59,60] in the course of time the "lower" layers in the boundary phase should be gradually enriched in the high-molecular-weight component. This should lead to an increase in the viscosity of the PMS in layers fairly close to the support.

Thus the viscosity of layers in the boundary phase is determined by the occurrence of two competing processes: ordered horizontal orientation of the linear molecules, which decreases the viscosity, and the increase in the concentration of the high-molecular component which increases it. In the series of PMS, the viscosity of the "lower" boundary phase of the PMS proved to be reduced in all the cases examined compared with the bulk phase. This means that the process involving the orientation of the molecules predominates and surface fractionation is hardly manifested owing to the narrow MWD of the PMS investigated.

The phenomenon of the fractionation of polymers with respect to molecular weights in the force field of the solid phase has been confirmed in a study of the boundary viscosity of binary mixtures of PMS having different molecular weights with the polydimethylsiloxane liquid PMS-10. The flow velocity profiles of films of these mixtures (Fig.15) differ significantly from the profiles of the films examined previously. They are characterised by the presence of steps in

the range of thicknesses 10–30 Å. The overall form and height of the steps are readily reproducible in replicate experiments and are independent of the molecular weight of the dissolved PMS. It is essential to note that the stepwise profile is obtained when the blowing off is carried out after the film of the test liquid has been maintained for 30 min on the suport. The stepwise profile of the film is not a consequence of its instability, since its form is retained after the blown off film has been kept for 1.5 h with certain intermediate measurements. Steps on the flow velocity profiles of films of binary PMS mixtures (Fig.15) show that in the region adjoining the support there are layers of liquids with an enhanced viscosity which are formed as a result of the enrichment of the boundary layer in the high-molecular-weight components of the mixture,[59,60] i.e. as a result of the surface fractionation of the polymer.

The increase in the viscosity of the boundary layer may indicate the occurrence in the polymer of processes associated with the change (expansion) of the MWD by external influences such as thermo- and photo-oxidation. It is known[61–63] that these processes lead to the cross-linking of the PMS macromolecules resulting in the formation of a gel. The accumulation of the oxidation products at an early stage of the process should alter the MWD and correspondingly the shape of the flow velocity profile of the film. As can be seen from Fig.16, the profiles of the PMS-200 films after thermo-oxidation differ from the initial films by the presence of steps or slip planes in the range of thicknesses up to 20 Å. The height of the steps remains stable throughout the series of experiments regardless of the degree of oxidation. With increse in the degree of oxidation, layers with enhanced viscosity become more distinct in the film profile. On the other hand, judging from the slope of the curves, the bulk viscosity does not change significantly.

In the photo-oxidation of PMS-200, a pattern analogous to that described above is observed (Fig.17): steps and slip planes appear on the film profiles of the liquid subjected to photo-oxidation for 12 and 48 h (curve *3*), such steps and planes being absent from the initial specimen. The bulk viscosity then increases appreciably with increase in the oxidation time and, in contrast to the previous case, is more sensitive to irradiation than the viscosity of the boundary layer.

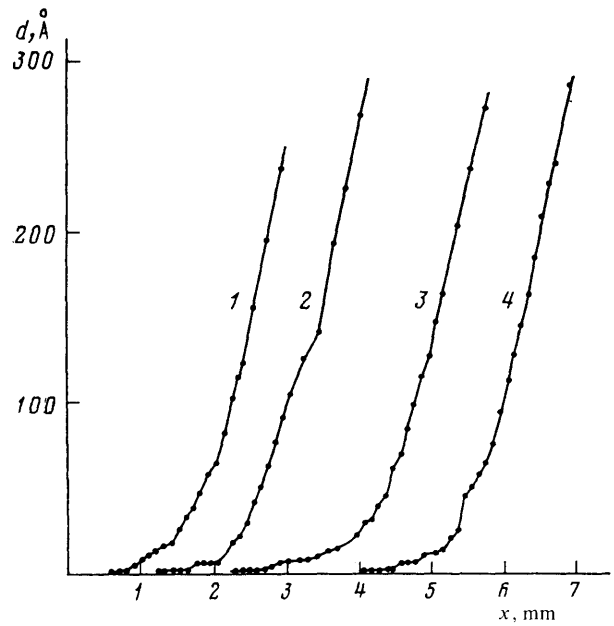


Figure 16. Profiles of PMS-200 films subjected to thermo-oxidation: 1) initial PMS-200; 2) PMS-200 oxidised for 15 h; 3) PMS-200 oxidised for 30 h; 4) PMS-200 oxidised for 45 h.

In both cases (in the thermo- and photo-oxidation of films), together with the stable elements of the profile (steps and slip planes), random bends appear on the velocity profiles which apparently reflect the random structural fluctuations in the polymer manifested in the blow-off process and caused by the presence of polar oxidation products. The formation of an adsorbed layer approximately 6 Å thick, firmly bound to the support, may be noted as a distinctive feature in the case of photo-oxidation.[55,57,58] Presumably this layer is made up of molecules of the test liquid chemisorbed on

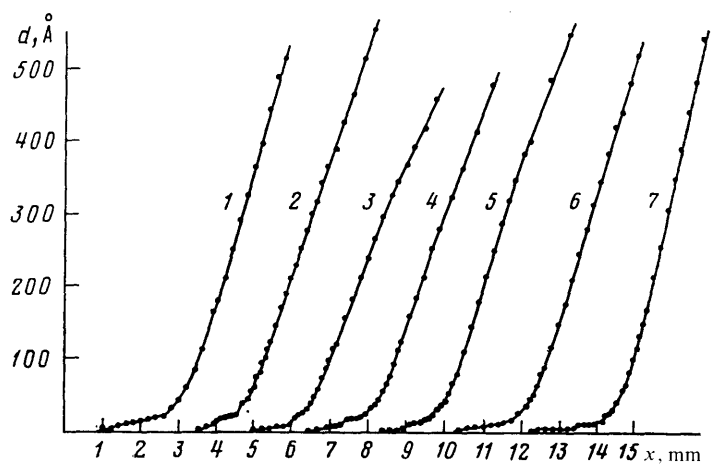


Figure 15. Film profiles for binary PMS mixtures: 1) PMS-10; 2) PMS-10 + PMS-70; 3) PMS-10 + PMS-400; 4) PMS-10 + PMS-2000; 5) PMS-10 + PMS-20 000; 6) PMS-10 + PMS-50 000; 7) PMS-10 + PMS-1 000 000.

the surface of the support by virtue of the presence in them of peroxy-radicals (CH_2OO or other reactive groups), formed as a result of oxidation processes initiated by UV radiation. This layer can be removed from the support only by repolishing its surface.

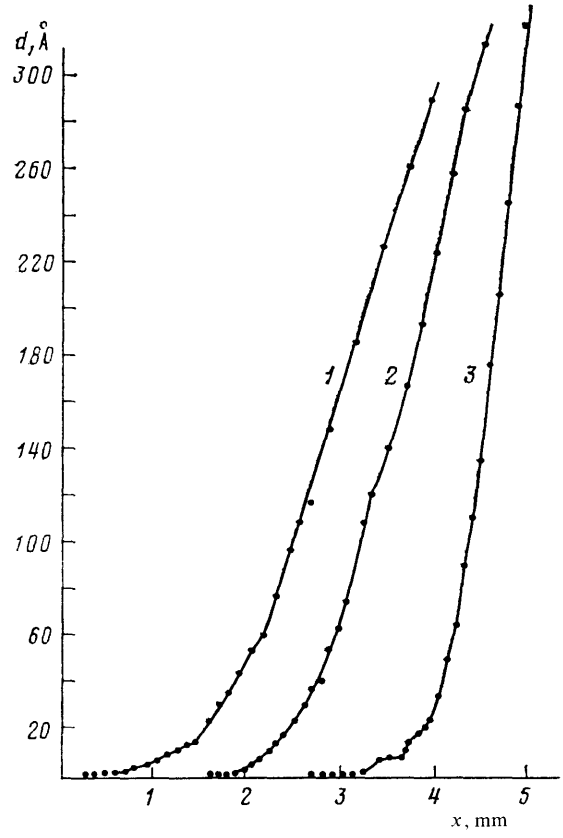


Figure 17. Profiles of PMS-200 films subjected to photodegradation: 1) initial PMS-200; 2) PMS-200 oxidised for 12 h; 3) PMS-200 oxidised for 48 h.

The substitution of methyl groups at the silicon atoms by groups of other chemical nature alters both the level and character of the intermolecular interaction and the degree of flexibility of the molecular chain.[57,58] It was shown earlier[50] that the introduction of polar β-cyanoethyl subsituents into the PMS molecule is accompanied by an appreciable increase in the level of intermolecular interaction as a result of the formation of a fluctuating network of bonds between the polar groups of neighbouring molecules. The flexibility of the molecular chains does not change significantly, which indicates an influence on the behaviour of such polymers in the vicinity of the surface of the solid. Indeed, in the presence of methyl-β-cyanoethylsiloxane units (Fig.18), an increase in the thickness of the boundary layer with an enhanced viscosity on average up to 60 Å is observed. Above 60 Å, the viscosity corresponds to the bulk phase value. It was found that the character of the flow velocity profiles of the film depends on the number of β-cyanoethyl groups. A smooth decrease in viscosity in the boundary layer is characteristic of liquids containing 6 and 100 mole% of methyl-β-cyanoethylsiloxane units (Fig.18, curves *1* and *6*). In the presence of 12.5 and 50 mole % of polar substituents (curves *2*–*5*), the appearance of slip planes at distances of 20 and 40 Å from the support is observed.

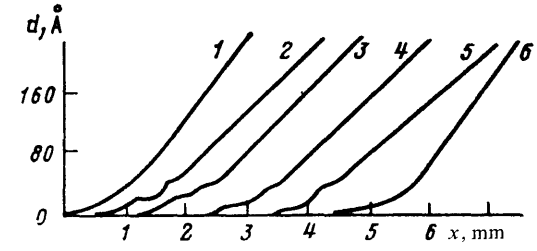


Figure 18. Profiles of films of dimethyl-β-cyanoethylsiloxanes with different contents of β-cyanoethylsiloxy-units: 1) PMS-6.25; 2) and 3) PMS-12.5; 4) and 5) PMS-50; 6) PMS-100.

In contrast to PMS, in dimethyl-β-cyanoethylsiloxanes the polar β-cyanoethyl groups are the centres of attraction to the surface of the support. One can therefore assume that in the given case the molecules are fixed on the surface of the solid phase via these groups. Depending on the number of polar groups, the conformation of the adsorbed molecule can be either extended parallel to the plane of the support or the molecule can have the form of a loop. When their content is low, these groups do not entail a significant change in the conformation of the adsorbed molecule compared with PMS. An analogous pattern has been observed also for a 100% content of methyl-β-cyanoethylsiloxane units (Fig.18, curve *6*). In these two cases, the molecules are adsorbed in a planar fashion, forming several layers, which are bounded by methyl groups and slip relative to one another. The film profiles of dimethyl-β-cyanoethylsiloxanes are therefore identical with the PMS film profiles both for slight and complete substitution of the dimethylsiloxane units.

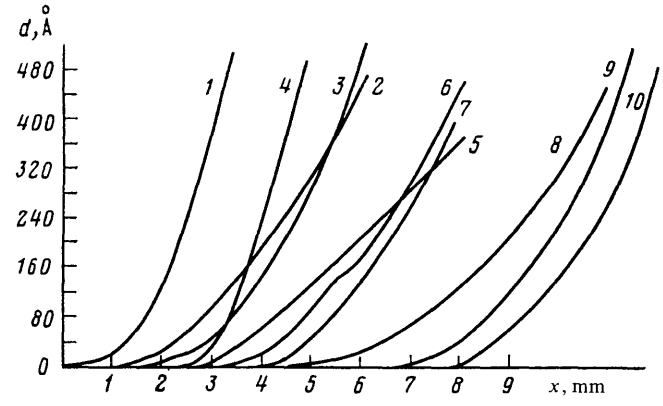


Figure 19. Profiles of films of oligo-organosiloxanes containing units of different types: 1) ethylsiloxy; 2) methylchlorophenylsiloxy; 3)–5) trifluoropropylsiloxy; 6)–9) thienylsiloxy; 10) chlorothienylsiloxy.

When the contents of the methyl-β-cyanoethylsiloxane units are 12 and 50 mole%, the molecules are adsorbed in such a way that the sections of the chains between the polar groups, linked to the surface, form loops which extend into the bulk of the liquid. The presence of slip planes at distances of 20 and 40 Å can apparently be explained by the formation of such structures.

The velocity profiles of films of oligo-organosiloxanes containing methylchlorophenylmethyl-, γ-trifluoropropyl-, thienyl-, and chlorothienyl-siloxane units (Fig.19) are outwardly identical with the film profits of dimethyl-β-cyanoethylsiloxanes, but the region of reduced viscosity extends in these substances to a greater depth (as far as 370 Å).[57,58]

The study of the surface and volume properties of a number of oligoorganosiloxanes[50,57,58] showed that the introduction of polar or bulky substituents reduces the intramolecular mobility. By virtue of this, the complete set of conformational transformations characteristic of polydimethylsiloxanes cannot be realised in the oligomers considered. The absence of an intermediate layer with enhanced viscosity, of the kind observed in PMS, is explained by this factor.

The distribution of polar groups along the molecular chain of oligo-organosiloxanes favours their horizontal orientation and adsorption on the surface. As in the case of the PMS, this reduces the viscosity in the boundary layer. On the other hand, the higher level of intermolecular interaction in oligo-organosiloxanes promotes the transmission of the influence of the force field of the solid phase into the bulk of the liquid to an appreciably greater distance than in the case of PMS. The region of reduced viscosity therefore reaches 350–370 Å in certain cases. The formation of slip planes in layers 20–30 Å thick in the oligomers considered (Fig.19, curves *2*, *3*, *6*, and *9*) can be attributed to their surface fractionation, intensified in the given instance by the presence of polar substituents at the silicon atoms and by the increased adsorption capacity of the molecules of these oligomers.[55,58]

Polydiethylsiloxane liquids in which the level of intermolecular interaction is enhanced compared with PMS occupy an intermediate position between oligo-organosiloxanes with polar groups and PMS as regards behaviour in boundary layers (Fig.19, curve *1*).[58]

It follows from the entire foregoing considerations that our flow velocity profiles of films indicate structural changes in the boundary layers. The observed anomalies in the profiles cannot be attributed to either the action of the capillary forces arising as a result of the microroughness of the support, or to the spontaneous migration of the wetting boundary, or to the surface tension gradients, because experiments with different liquids were not performed on the same support. Despite this, depending on the presence of polar groups, the degree of rigidity of the chain, and other factors, the flow velocity profiles of the films have their specific features, including the presence and absence of curvature in the range of thicknesses from zero to 50 Å. If the microroughness of the support had been the source of the anomalies in the profiles, then the latter would have appeared in all cases. Furthermore, the rate of spreading of the liquid under the influence of the microroughness is extremely low and the degree of spreading is 0.04 cm after 1300 s for the PMS with a viscosity of 0.07 St [64]# on a vertical plate, whilst according to our data a spreading of 0.06 cm was obtained for a PMS with a viscosity of 0.1 St on a horizontal plate after 5100 s. On the other hand, the blow-off experiments were performed over a short period and with viscous liquids. For example, the blowing off of PMS with a viscosity of 0.7 St was performed immediately after depositing the liquid on the support over 420–800 s.[65] The curving of the flow velocity profile of the liquid film was then observed at a distance of 0.3–0.4 cm from the wetting boundary. Judging from the data presented, this fact cannot be explained by the influence of the roughness of the support. Furthermore, the movement of the wetting boundary during the blow-off process was not observed in the experiments.

#Having observed conditions under which the blow-off method involves appreciable errors, Bascom and Singleterry[64] decided to abandon this method. Despite the subsequent explanation,[68] many investigators followed their example having decided to ignore a wide variety of results which we obtained. This is an example of how it is often difficult for a significantly new and novel development to achieve recognition.

V. THE STUDY OF THE BOUNDARY VISCOSITY OF ORGANIC LIQUIDS IN THE BLOW-OFF PROCESS

All the versions of the blow-off method described hitherto are suitable solely for liquids producing films which are stable in time. The blow-off method has been modified for the investigation of unstable films. For this purpose, a procedure has been developed for the observation of films in the course of the blow-off process.[29] The essential feature of the method is that the measurement of the film thickness is always performed at the same site and the dependence of the thickness on the blow-off time is obtained. The dependence of the boundary viscosity on the distance from the support is determined from the formula

$$\eta = \frac{H}{2}\frac{\Delta p}{\Delta l}\frac{dh}{du(h)} ,$$

where $\Delta p/\Delta l$ is the pressure gradient along the blowing off stream and $u = x/t$, x being the distance from the wetting boundary to the point of observation and t the time from the start of the blowing off to the measurement of the thickness h.

A glass apparatus was used for these experiments;[66] the slit was covered by a prism from which the beam emerged at a definite angle and fell on the insert with the film. In the study of boundary viscosity on glass, a total internal reflection prism was used and the film was deposited on the base of the prism.

A series of organic liquids, effectively wetting metals and glass, were investigated by this method. In the first place, the flow velocity profiles were obtained for liquid paraffin of different grades on a metal and glass. Metallic plates of ShKh-15 steel, polished to class 14 quality, were subjected to additional optical polishing. In all cases rigorously linear velocity profiles were obtained, indicating the absence of an unusual boundary viscosity. Velocity profiles were then recorded for solutions of stearic acid in liquid paraffin.[29,65–67] In order to obtain reproducible results on glass, the latter was cleansed in a gas discharge.[30] Appreciable distortions in the profile were observed at a stearic acid concentration of 0.000021 %. A linear profile with slight steps, whose number and height were not reproducible in different experiments, was obtained. At a concentration of 0.00054 %, an increase in the number of steps is observed (Fig.20) and they are appreciably more pronounced. Their height and number are likewise not reproducible. At a concentration of 0.001 %, inadequate wetting is observed, so that on being blown off the film breaks up into fine drops. This can be explained by the formation of an adsorption layer made up of molecules with vertically disposed methyl groups. At a concentration of 0.01 %, the wetting disappears completely and the solution drains off like water from a greasy surface. This occurs as a result of the completion of an adsorption monolayer of stearic acid, which is not wetted by virtually anything.

Solutions of hydrocarbons, consisting mainly of tetracosane ($C_{24}H_{50}$) with chlorinated methylene groups in the middle section of the chain (mono-, tri-, hexa-, and dodeca-chloroparaffins), in liquid paraffin were tested next.[28,65-67] Steel plates additionally polished and cleaned in a gas discharge in argon served as the supports. In the first place, the velocity profiles were obtained for a solution of monochloroparaffin in D-1 liquid paraffin, after its purification in a chromatographic column, and in liuquid paraffin subjected to acid-alkaline purification. It is seen from the plots (Fig.21*a*) that in the given instance a boundary layer with a modified viscosity, having a thickness of approximately 200 Å, is produced. Trichloroparaffin dissolved in liquid paraffin (Fig.21*b*) yields a result similar to the previous one: a boundary layer approximately 300 Å thick is observed near the wall. The results of the study of the solution of hexachloroparaffin are presented in Fig.21*c*. In this case a velocity profile resembling the previous ones was obtained. A change in viscosity is likewise observed in a boundary layer approximately 250 Å thick. Measurements with dodecachloroparaffin could not be performed because of the absence of wetting.

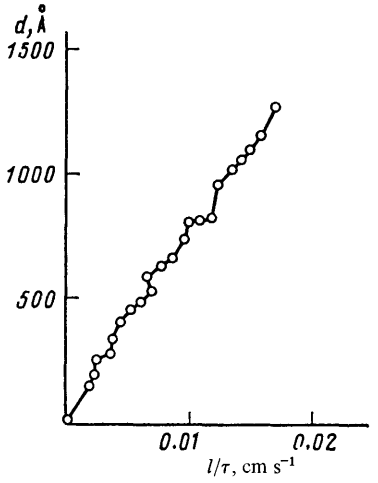


Figure 20. Prifile of a film of 0.00054 % solution of stearic acid obtained on a glass surface during the blow-off process.

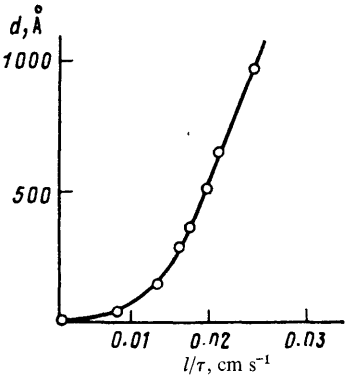


Figure 22. Flow velocity profile of a film of incompletely hydrogenated benzanthrone obtained on a glass surface during the blow-off process.

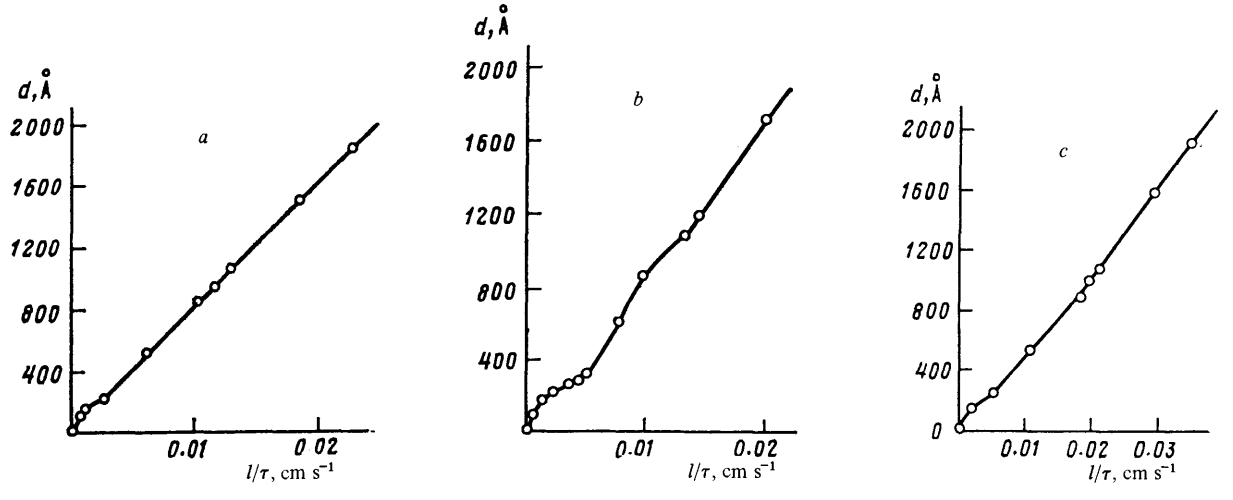
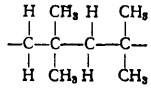


Figure 21. *a*) Profile of a film of 0.01% solution of monochlorotetracosane in liquid paraffin obtained on a steel surface during the blow-off process; *b*) profile of a film of 0.01% solution of trichlorotetracosane in liquid paraffin obtained on a metallic surface during the blow-off process; *c*) profile of a film of 0.01% solution of hexachlorotetracosane obtained on a glass surface during the blow-off process.

Finally, certain individual liquids were blown off. The flow velocity profile was obtained initially (on glass) for the incompletely hydrogenated benzanthrone.[48]§ As the name shows, this substance is not strictly individual. At the start of the experiment, the film was allowed to stand in order that equilibrium should be established in thin layers. Fig.22 illustrates the velocity profile, from which it is seen that, in the immediate vicinity of the wall, the viscosity is appreciably reduced. Above 200–300 Å (naturally this is a very arbitrary figure, since the viscosity varies very smoothly), the viscosity is almost equal to the bulk phase value.

The latest object was polyisobutene, which can be represented by the following formula, for example:



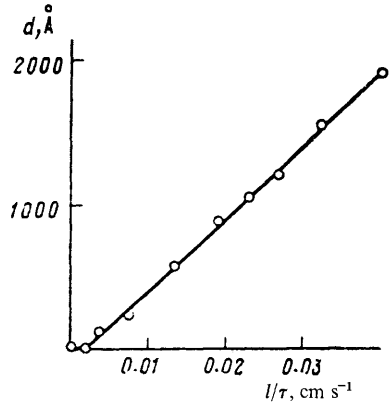


Figure 23. Flow velocity profile of a film of polyisobutene obtained on a metallic surface during the blow-off process.

It is seen from Fig.23 that the velocity profile is close to a linear one; a slip can be seen near the wall. The thickness of the residual film could not be measured. The measurements were performed on a steel plate.[28]

VI. THE STUDY OF THE BOUNDARY VISCOSITY OF VOLATILE LIQUIDS

A limitation of the blow-off method has been hitherto the impossibility of applying it to the study of the boundary viscosity of volatile substances. A modified blow-off method is applicable also to such liquids. In the course of the blowing off of volatile liquids, the film is attenuated also as a result of evaporation. The corresponding theory and method of calculation of the viscosity have been developed by Deryagin and Starov.[34] The viscosity calculations were performed on a computer from the ellipsometrically measured thicknesses of the blown off film at a distance of 2 cm from the initial wetting boundary as a function of time.

The apparatus with a rectangular insert on which the experiment was performed did not differ from the previous ones used to investigate the boundary viscosity by the blow-off method. Hexadecane ($C_{16}H_{34}$), an industrial product of chemically pure grade, was chosen as the test liquid. Specimens subjected to different degrees of chromatographic purification were also tested.

The experiment was performed as follows: a layer of liquid was deposited on the insert as before. Theinset was placed in the apparatus, having determined exactly the position of the wetting boundary, and a stream of air was passed through. The film thickness was determined as a function of time at a fixed site, at a distance l = 20 mm from the wetting boundary; the pressure drop was Δp = 0.0184 mmHg. The corresponding shear stress was 0.4 dyn cm^{-2}. The film thickness was measured as a function of time on an elipsometer using an LG-56 gas laser. Fig.24 presents plots of the dependence of the viscosity on the distance from the support obtained, from which it is seen that the viscosity is reduced in the range of thicknesses from 50 to 200 Å. The reproducibility of the curves in the range of thicknesses as far as 250 Å is complete in different experiments.[34]

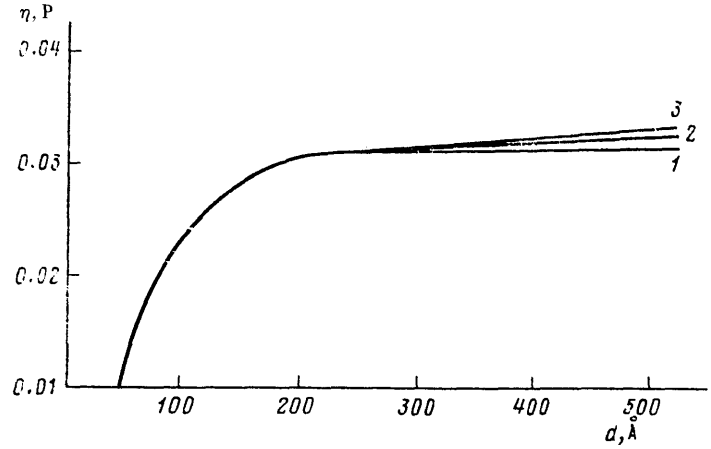


Figure 24. Dependence of the viscosity of hexadecane on the distance from the support.

§This substance was synthesised in A.D.Petrov's laboratory.

The decrease in viscosity which we observed can probably be accounted for by the usual slip of the horizontally oriented molecules. The hexadecane molecule consists of 14 methylene and 2 terminal methyl groups. In the immediate vicinity of the wall, one may expect only a horizontal orientation of the molecules because of their rigidity and fairly considerable length. The horizontal orientation is gradually enhanced as the support is approached owing to the increase in the influence of the force field of the latter.

The results of the application of the blow-off method described show that it provides a unique possibility for discovering the characteristic features of the structure of liquid layers modified under the influence of the adjoining surface of a solid phase, which is reflected by changes in viscosity. Specially rich information is provided by the application of the method to polymers and their solutions. The influence of the support on the structure of the boundary layers of the polymers and also on the stability of the wetting films is observed in this case to a strikingly greater depth, amounting to several micrometers.

Further expansion of the region where the method is applicable will become possible if the procedure can be improved in such a way that evaporation of even a highly volatile liquid can be eliminated during the blowing off of the layer.

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Reactions of Saturated Cyclic Sulphides

E.N.Karaulova

The latest advances in the chemistry of saturated cyclic sulphides, mainly with 3-10-membered rings and their derivatives are examined. The results of studies concerning the introduction of functional groups into the sulphides and the conversion of the sulphides into acyclic compounds are surveyed.
The bibliography includes 198 references.

CONTENTS

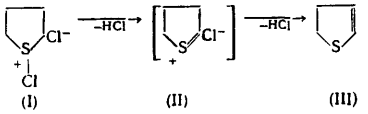
I.	Introduction	648
II.	Complexes involving cyclic sulphides	648
III.	Oxidation of the sulphides	649
IV.	Reactions with opening of the heterocycle	651
V.	Rearrangements with change in the number of members in the ring	653
VI.	Polymerisation of cyclic sulphides	657
VII.	Thermolysis and fragmentation of cyclic sulphides	658
VIII.	Dehydrogenation and desulphurisation of cyclic sulphides	658
IX.	Photochemical reactions of the sulphides	659
X.	Introduction of functional groups without change in the carbon skeleton	660
XI.	The synthesis and reactions of cyclic sulphonium salts	661

I. INTRODUCTION

During the last 10–15 years the reactions of cyclic sulphides such as sigmatropic rearrangements and reactions with ring opening have found extensive applications in synthetic organic chemistry. New data have been obtained on "traditional" reactions—complex formation and oxidation. The synthesis and the reactions of sulphonium salts have developed vigorously. They are promising for use in the chemistry of dyes and as fungicides and flocculants. Zwitter-ions based on arylthioniacycloalkane salts have found applications as monomers for the preparation of polymers stable in water and acids. The review covers the literature up to 1986, mainly during the last 10 years. Earlier data are described in monographs[1,2] and other reviews.[3-5]

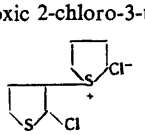
II. COMPLEXES INVOLVING CYCLIC SULPHIDES

Thiolan reacts with chlorine to form the 1:1 complex (I), which is stable in methanol only at a low temperature.[6] On raising the temperature of the complex (I), Pummerer's reaction takes place with the tentative formation of the carbosulphonium ion (II), which undergoes further reactions:[7]



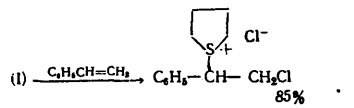
(I) (II) (III)

The dihydrothiophen (III) formed under these conditions adds to the complex (I), affording the toxic 2-chloro-3-thiolanylthiolanium chloride (IV):



(IV)

Hydrogen chloride retards the decomposition of the complex (I), possibly inhibiting the formation of compound (II). The complex (I) reacts with unsaturated compounds giving rise to sulphonium salts; the reaction proceeds effectively with styrene:[7]



The charge-transfer complexes formed by thiolan, thiane, and 1,4-dithiane with iodine absorb in the far IR at the following frequencies respectively: 158, 200 cm^{-1}; 157, 214 cm^{-1}; 165 cm^{-1}, while the complexes of the same sulphides with iodine bromide absorb at 186–188 and 222–228 cm^{-1}.[8]

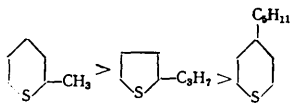
Saturated cyclic sulphides form donor–acceptor complexes with participation of a hydrogen bond with hydroxyl-containing compounds. When they are absorbed on silica and alumina, thiolan and thiane form hydrogen bonds with the hydroxy-groups of the sorbents and there is also an interaction with the electron-accepting centres on the alumina surface.[9] The thermodynamic characteristics of the complexes of thiolan with phenols have been determined: $\Delta H = -3 \pm 0.2$ kcal mol^{-1} and $\Delta S = -9.4$ kcal mol^{-1} K^{-1} for the hydrogen bond in the thiolan–phenol complex, while for the complex of thiolan with resorcinol we have $\Delta H_1 = -4.6 \pm 0.8$ kcal mol^{-1} and $\Delta S_1 = -13$ kcal mol^{-1} K^{-1}.[10]

The ability of sulphides, including cyclic sulphides, to form complexes with mercury(II) acetate has served as the basis of the acidimetric method for the quantitative potentiometric determination of sulphides.[11]

The stability of thiolan complexes (and also *d*-biotin complexes) with biologically important metal ions (Mg^{2+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) and also with Ag^+ in 50% alcohol, 96% dimethylformamide (DMF), and 98% dimethyl sulphoxide (DMSO) or D_2O) is extremely low; with increase in the concentration of water, the interaction of the sulphides with all the ions except Ag^+ increases.[12]

In order to model the capacity of petroleum sulphides for extraction from K_2ReOCl_5 solution, 13 complexes of 2-propylthiolan, 2-methylthiane, and 4-pentylthiane having the composition $L_2Re(=O)Cl_3$, where L = thiacycloalkane, have been obtained.[13] They have the structure of a flattened octahedron, where the chlorine atoms and one of the ligands are located in the equatorial

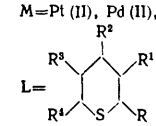
plane, while the oxygen and the second sulphide molecule occupy the vertices of the octahedron. The energy of formation of the complexes and their thermal stability diminish in the sequence of ligands



Acido-complexes with bivalent platinum and palladium salts have been obtained from aryl- and alkyl-substituted thianes, thiadecalins, and perhydrothioxanthenes:[14,15]

$$2L + K_2MCl_4 \xrightarrow{\text{alcohol}} ML_2Cl_2$$

M=Pt (II), Pd (II),



$R=R^4=C_6H_5$, $R=R^4=C_4H_5$, $R^2=CH_3$; $R=R^3=R^4=C_6H_5$; $R=C_6H_5$, $R^3R^4=(CH_2)_4$; $R=R^3=C_6H_5$, $R^3R^4=(CH_2)_4$; $RR^1=R^3R^4=(CH_2)_4$; $R^1=R^3R^4=(CH_2)_4$, $R^2=CH_3$; $RR^1=R^3R^4=(CH_2)_4$, $R^3=C_6H_5$.

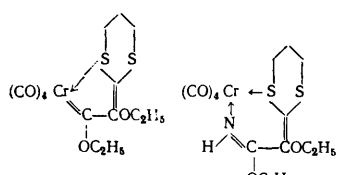
On crystallisation from benzene, the last two compounds give rise to $PtL_2Cl_2.C_6H_6$ and $PtL_2Cl_2.2C_6H_6$ respectively. The complexes exhibit a moderate antimicrobial activity; the complexes of bicyclic and tricyclic sulphides show a more appreciable antiphage activity.[14] The complexes of PdL_2Br_2 having the *trans*-configuration have been obtained in 83–94% yields from PdL_2Cl_2 and KBr in aqueous acetone;[15] the complexes PtL_2X_2 have been obtained in aqueous dioxan:

$$L + K_2PtCl_4 + KX \xrightarrow{\text{aqueous dioxan}} PtL_2X_2 ;$$

X = Br, I; L = 2,6-diphenyl, 4-methyl-2,6-diphenyl-, or 2,4,6-diphenylthiane.

The complex of palladium chrloide with 4-methyl-2,5-diphenylthiane has been used[16] as the catalyst in the dehydrohalogenation of 3,4-dichlorobut-1-ene.

The chelates (V) and (VI) have been obtained from 1,3-dithiane:[17]



(V) (VI)

The formation of complexes by macrocyclic sulphides, especially thiacrown-ethers, has been investigated in recent years (for a review of the complexes between sulphides and transition metals, see Murray and Hartly[18]). Complexes of 1,4,7-trithiacyclononane with univalent copper, nickel, and cobalt tetrafluoroborates have been obtained; the metal atom in these complexes is at the centre of a slightly deformed octahedron. The complexes of 1,4,8,11,tetrathiacyclotetradecane (VII) with rhodium and cobalt salts, i.e. $[Rh(VII)X_2]^+$ and $[Co(VII)X_2]^+$, where X = Cl, Br, NCS, NO, or $1/2Cr_2O_4$, have been investigated. The cobalt complexes are obtained in three ways: from a bivalent cobalt salt with a non-coordinating anion and the sulphide, this step being followed by the reaction of the resulting complex with a coordinating anion and oxidation with air; from a cobalt salt, the sulphide, and an anion accompanied by oxidation in a single stage; in a complex with tervalent cobalt by exchange with a more strongly coordinating anion.[20]

The rhodium complexes have the *cis*-structure. The magnetic moments, molecular conductivities, and absorption IR and visible spectra have been measured for the complexes enumerated above.[20]

The cation $[Rh(VII)]^+$ has been obtained[21] by reducing the rhodium complexes and its capacity for coordination to various anions and electrophiles has been investigated. The cation $[Rh(VII)]^+$ enters into oxidative addition reactions, for example, with acetyl chloride, which involves an increase in the coordination number of rhodium and in its oxidation state (up to Rh^{2+}).

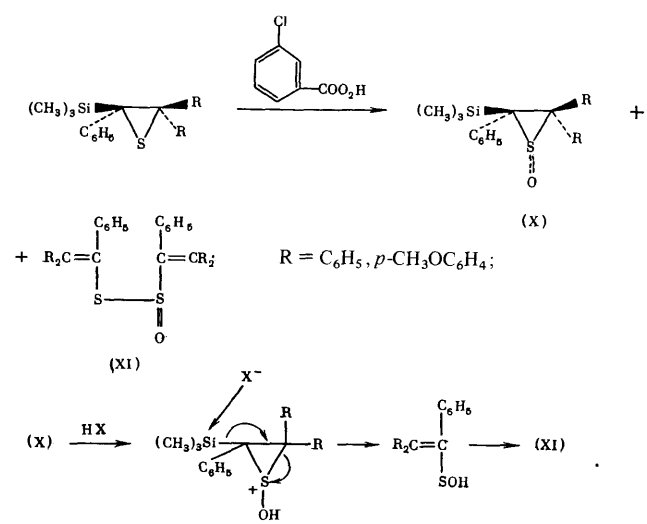
The extracting capacity of the thiacrown-ether (VII) in relation to the cations Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Te^+, Ag^+, Pd^{2+}, Cd^{2+}, and Hg^{2+} (anions—perchlorate, picrate, and tetraphenylborate) has been investigated.[22] Only copper is extracted quantitatively. The complexes of pentathia-15-crown-5-(1,4,7,10,13-pentathiacyclopentadecane) (VIII) with univalent and bivalent copper have been obtained.[23] The electrolytic reduction of the $[Cu(VIII)]^{2+}$ complex in a nitrogen atmosphere leads to $Cu[(VIII)]^+$. Both complexes are monomeric in the crystalline state.

The complex with Cu^{2+} has a square-pyramidal geometry with the copper atom located 0.41 Å above the basal plane, which is made up of four electron-donating sulphur atoms, the fifth sulphur atom being coordinated at the vertex but deviating by 12.8° from the perpendicular. The Cu^+ complex has the structure of a distorted tetrahedron, close to the geometry of the complex with Cu^{2+} but with the exception that one of the C–S bonds in the basal plane is impaired. In both complexes, the perchlorate anions are not coordinated.

The complex of 1,4,7,10,13,16-hexathiacyclo-octadecane (hexathia-8-crown-6) (IX) with nickel picrate (1 : 1) is obtained[24] by refluxing in acetone. The octahedral complex $[Ni(IX)]^{2+}$ has a star structure: the nickel ion is at the centre of symmetry and the thiacrown ether surrounds it.

III. OXIDATION OF THE SULPHIDES

The oxidation of thiirans and substituted phenylthiiran oxides by peroxide compounds has been discussed in a monograph.[2] When *cis*-2,3-diphenylthiiran is oxidised with perbenzoic acid, the *anti*-sulphoxide is formed exclusively.[25] When silylated thirrans are subjected to similar oxidation, they give rise to ring opening products together with the sulphoxide (with the *anti*-disposition of the S=O group relative to the silyl group), possibly as a result of the acid-catalysed conversion of the sulphoxide (X) into an unstable sulphenic acid, which dimerises with simultaneous dehydration:[26]

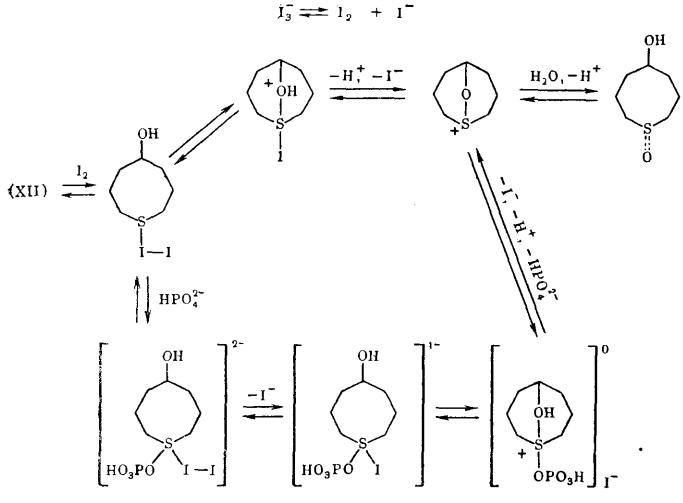


(X) (XI)

The alternative homolytic opening of the ring in compound (X) is not, however, ruled out.

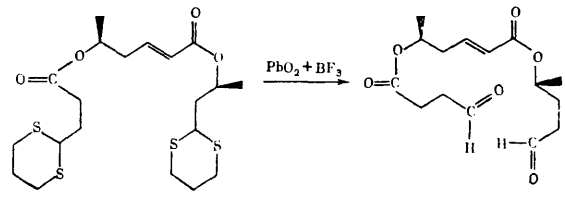
Tetrafluoromethyl-1,3-dithietan is oxidised by chromium trioxide or nitric acid to the monosulphone.[2]

Thiolan is converted into cyclobutane when it is ozonised in oxygen.[27] The oxidation of thiolan to the sulphoxide by gaseous oxygen is catalysed by petroleum metalloporphyrins, most effectively by vanadyl-porphyrins.[28] When thiolan and thiane are oxidised with atmospheric oxygen in the presence of copper(II) dichloride (in isopropyl alcohol at 130 °C and 50 atm),[29] sulphoxides are formed in 50–70% yields and a selectivity of 70–80%; 2-hexytlthiolan is not oxidised under these conditions. Thiolan and thiane are oxidised to the sulphones by refluxing with a solution of copper(II) permanganate or a mixture of potassium permanganate and copper(II) sulphate pentahydrate.[30] 2,5-Dichloromethylthiolan and 2-chloromethyl-5-chlorothiane were oxidised to the sulphoxides with t-butyl hydroperoxide in the presence of $MoCl_5$;[31] 1,3,5,7-tetramethyl-2,4,6,8-tetrathia-adamantane was oxidised in the same way (in benzene) to the 2-oxide in 55% yield.[32] The oxidation of 4-hydroxythiane, 4-hydroxy-4-methylthiane, and 5-hydroxythiacyclo-octane (XII) with iodine in aqueous methanol in the presence of phosphate buffer takes place with participation of the *trans*-annular interaction of the hydroxyl with sulphur;[33] in the case of the sulphide (XII), the bridged intermediate 9-oxa-1-thioniabicyclo[3.3.1]nonane tri-iodide was isolated (not shown in the scheme below) whose oxidation leads to hydroxysulphoxides with a great preponderance of the stereoisomers having the OH and S=O groups in the *trans*-positions (in excess of 92%). Under these conditions, the sulphide–iodine complex is initially formed from the tri-iodide and then decomposes via two pathways, the main pathway depending on the buffer and its reverse process being of second order with respect to the iodide:

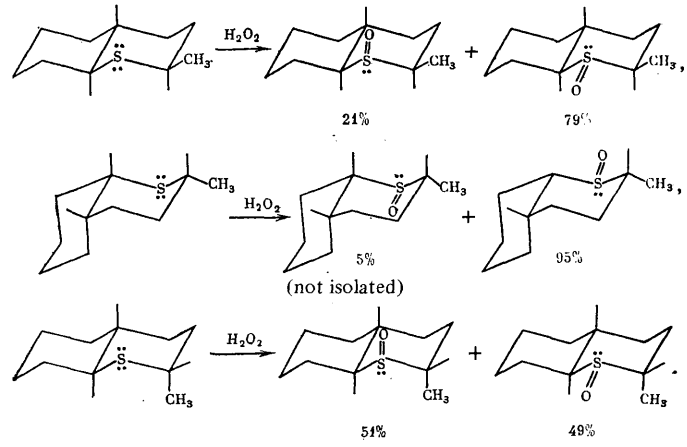


The electrochemical oxidation of 4-(*p*-chlorophenyl)thiane in aqueous acetone or acetonitrile in the presence of bromides, for example, $(C_4H_9)_4NBr$, affords[34] isomeric sulphoxides in 80% yield (under the conditions of kinetic control, about 90% of the *trans*-isomer is formed and at equilibrium there is 80% of the *cis*-isomer). One of the sulphur atoms in 2-(α-tetrahydrofuryl)-1,3-dithiane is oxidised by sodium periodate,[34] the yield of the sulphoxide being 70%.

Treatment of 5-(*o*-carboxyphenylamino)-2-phenyl- and 5-(*o*-carboxyphenylthio)-2-phenyl-1,3-dithianes with hydrogen peroxide in acetic acid[36] gave rise to the corresponding bis-sulphones. Extensive oxidation hydrolysis of 1,3-dithianes has been used[37] in one of the stages of the synthesis of gramicidin:



The oxidation of the stereoisomers of 3-methyl-2-thiabicyclo[4.4.0]-decane with hydrogen peroxide in acetic acid[38] led to the isolation of the stereoisomeric sulphoxides:



The oxidation of thiadecalins and thiabicyclo[4.3.0]nonanes has also been discussed in the review.[5]

4-Thiahomoadamantane was oxidised[39] with *m*-chloroperbenzoic acid to the sulphone in 54% yield. 2-*exo*-Hydroxy-4-thiahomo-adamantane (XIII) was oxidised[39] with pyridinium chlorochromate to the corresponding ketone in 48% yield; together with the ketone, 3-thiatricyclo[5.3.1.$0^{4,9}$]undec-5-ene is formed as a result of skeletal rearrangement (with participation of the episulphonium ion).

It is appropriate to consider also the oxidation of petroleum sulphides, since saturated cyclic sulphides predominate among them.[1] The oxidation of the petroleum sulphides to sulphoxides is the principal method of converting them into derivatives with functional groups. In the liquid-phase oxidation with atmospheric oxygen in the presence of copper chloride in isopropyl alcohol (heating under pressure),[40] the degree of conversion of the petroleum sulphides does not exceed 90% and the maximum selectivity is then 80% (for a yield of about 70 mole %). When the concentrate of petroleum sulphide is oxidised with oxygen in the presence of copper phenoxide, the formation of sulphoxides is inhibited by the competing reaction involving the oxidation of the hydrocarbons present in the concentrate.[41] The oxidation of petroleum sulphides to the sulphoxides directly in petroleum distillates can be usefully performed with t-pentyl. t-butyl, and cumenyl hydroxperoxides;[42,43] the highest conversions are obtained in oxidation catalysed by molybdenum compounds in the presence of carboxylic acids.[43] Molybdenum naphthenate has been recommended[44] as the catalyst for the oxidation of petroleum sulphides to the sulphoxides with hydrogen peroxide.

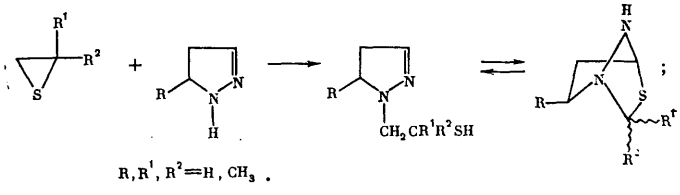
The concentrates of petroleum sulphides have been oxidised to the sulphoxides with a mixture of air and nitrogen dioxide.[45] The method can be regarded as successful, since a complex mixture of

nitrogen-containing products is formed together with the sulphoxides.

IV. REACTIONS WITH OPENING OF THE HETEROCYCLE

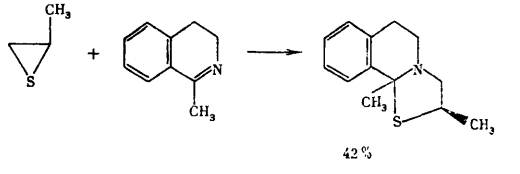
1. The Effect of Nucleophiles

When thiiran and its methyl-substituted derivatives react with unsaturated cyclic nitrogen-containing bases, the thiiran ring is opened in accordance with Krasuskii's rule.[46,47] The reaction with 2-pyrazolines results in the formation of 1-(2-mercaptoalkyl)-2-pyrazolines, which are capable of isomerising reversibly to 4-thia-1,8-diazabicyclo[3.2.1]octanes.[46] A mixture of diastereoisomeric mercaptoalkylation products in comparable amounts is formed from 5-methyl-2-pyrazoline:



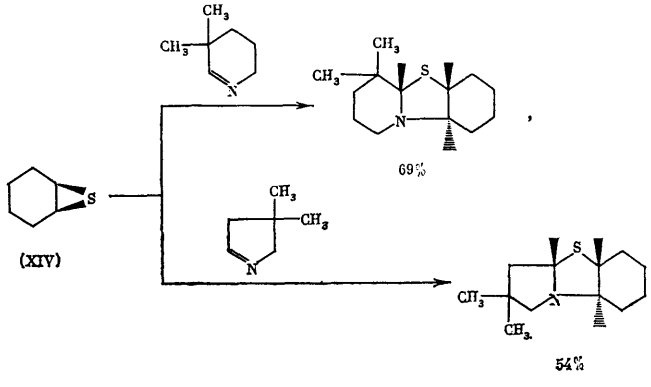
R, R', R²=H, CH_3 .

The reaction with 2,3,4,5-tetrahydropyridines and 1-pyrrolines affords the corresponding perhydrothiazolo[2,3-*a*]pyridines and perhydropyrrolo-[2,1-*b*]thiazoles.[47] In the case of methylthiiran, compounds with the *cis*-disposition of the angular substituent and the methyl group are formed:



42%

In the reaction involving epithiocyclohexane (XIV), the opening of the thiiran ring is accompanied by the inversion of the configuration:[47]

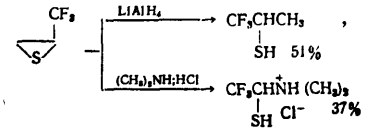


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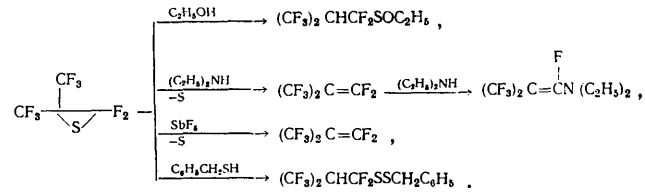
54%

(XIV)

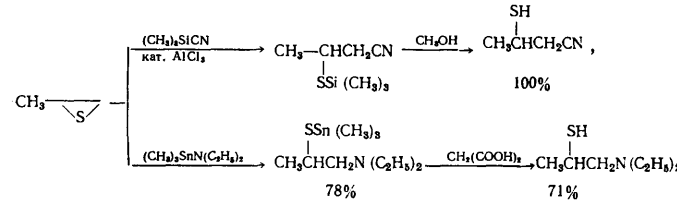
The aminomercaptans $C_4H_9OCH_2CH(SH)CH_2NRR^1$ (R = R^1 = C_4H_9; R = C_6H_5, R' = CH_3) have been synthesised[48] by treating butoxymethylthiiran with amines. Nucleophiles act analogously on trifluoromethylthiiran:[49]



In contrast to this, in the case of perfluorothiiran the attack by the nucleophile is directed to the sulphur atom:[50]

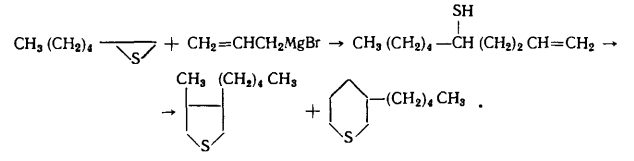


Regioselective opening of the thiiran ring occurs on treatment of organic derivatives of Group IVB elements,[51] such as $(CH_3)_3SnNR_2$ and $(CH_3)_3SiCN$. The subsequent alcoholysis or acidolysis of the reaction products leads to β-amino- or β-cyano-thiols:

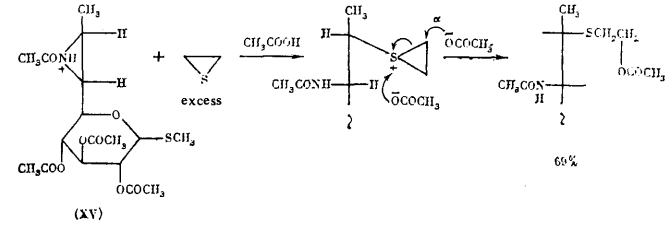


78% 71%

The reaction of thiirans [including epithiocyclohexane (XIV)] with alkenylmagnesium bromides is of great synthetic importance. It yields alkenethiols, whose subsequent cyclisation leads to five-membered and six-membered thiacycloalkanes,[52–54]† for example:[52]

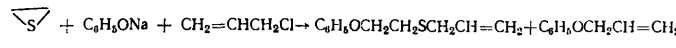


Treatment of tetra-acetylepimine (XV), a derivative of the antibiotic linocomycin, with thiiran in acetic acid affords the 7-(2-acetoxyethyl)thio-derivative:[55]



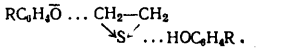
(XV)

The opening of the thiiran ring by phenols under the conditions of base catalysis leads to the polymerisation of the thiiran; in order to suppress it, a powerful electrophile (allyl chloride) is introduced:[2,56–59]

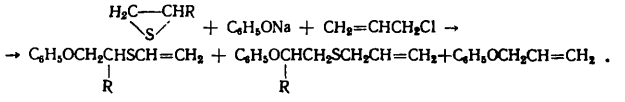


† For a detailed description see Karaulova's review.[4]

The study of the kinetics of the reaction led to the conclusion[56] that its mechanism involves the formation of complexes of sodium phenoxide with thiirans. In the case of substituted phenoxides RC_6H_4ONa (R = *p*-CH_3, *p*-OCH_3, *m*-CH_3, *p*-F, *p*-Cl, *p*-I, or *m*-Cl), the rate of ring opening diminishes as the electron-accepting properties of the substituent are enhanced, but the rate increases as the acidity of the phenol is reduced (by introducing electron-donating substituents).[57] The ring opening is achieved as a result of the joint action of the nucleophile and the proton donor:

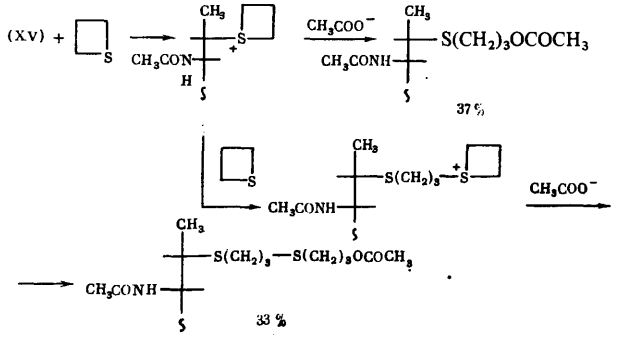


In the reaction of substituted thiirans, the mode of opening of the thiiran ring varies as a function of the electronic character of the substituent:[58]



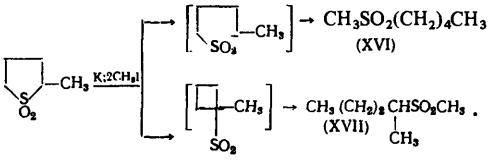
For substituents whose electronic effect is transmitted via the inductive mechanism, products corresponding to the opening of the ring in accordance with Krasuskii's rule predominate (R = CH_3, 75%; R = CH_2OCH_3, 96%; R = C_4H_9, 75%). For substituents containing a π-electron system, anomalous reaction products predominate (R = C_6H_5, 80%; R = $CH{=}CH_2$, 90%). The reaction with disubstituted thiirans proceeds analogously;[59] in highly polar aprotic solvents, the rate and regioselectivity of the reaction increase sharply.[59]

Thietan in acetic acid reacts with the tetra-acetylepimine (XV) via two pathways:[55] the formation of the 7-(3-acetoxypropyl)thio-derivative is accompanied by the interaction with a second thietan molecule:

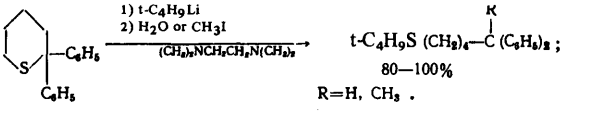


Thiolan and thiane react with compound (XV) only via the first pathway[55]—the 7-(4-acetoxybutyl)thio-derivative (yield 71%) and the 7-(5-acetoxypentyl)thio-derivative (yield 11%) are formed respectively.

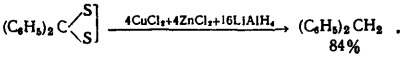
Colloidal potassium (obtained by dispersing potassium in toluene by exposure to ultrasound) is an effective reagent for the clevage of the C–S bond.[60] Its effect on sulphone derivative from thietan, thiolan, 2-alkylthiolans, and thiane has been investigated. The yields of alkyl methyl sulphones are 84–94%. It has been shown for 2-methylthiodioxide that the reaction is regioselective—cleavage of the C–S bond takes place mainly at the substituted carbon atom [we have the ratio (XVI):(XVII) = 10:1]:



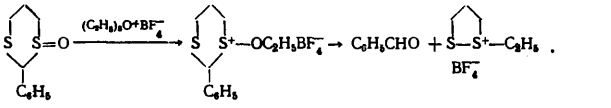
The ring of 2,2-diphenylthiane is ruptured analogously on treatment with t-butyl-lithium:[61]



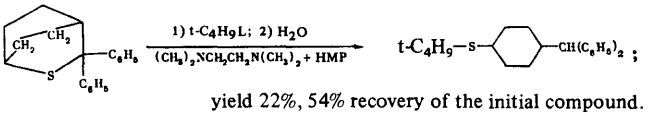
The reductive cleavage of the C–S bond at C(2) in 2,2-diphenyl-1,3-dithiolan takes place on treatment with lithium tetrahydroaluminate in combination with copper and zinc chlorides:[62]



Intramolecular decomposition has been observed[63] on treatment of 2-phenyl-1,3-dithiane-1-oxide with triethyloxonium tetrafluoroborate:[63]



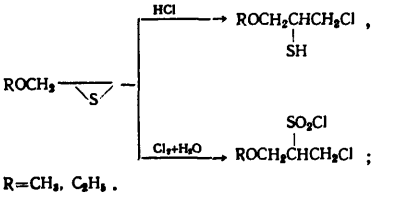
The rupture of the C–S bond in the 3,3-diphenyl-2-thiabicyclo-[2.2.2]octane on treatment with t-butyl-lithium proceeds with difficulty:[61]



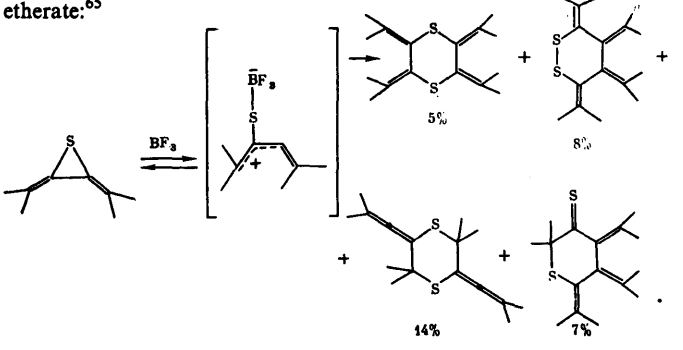
yield 22%, 54% recovery of the initial compound.

2. The Effect of Electrophiles

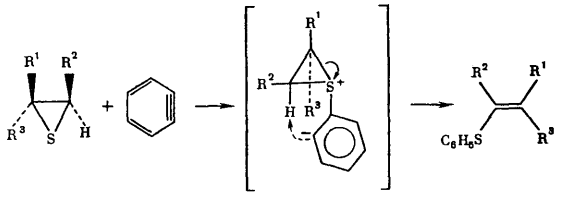
2-Alkoxymethylthiirans react with hydrochloric acid at low temperatures or with chlorine in accordance with Krasuskii's rule:[64]



Diallene episulphide ("thiiranoradialene") produces (together with polymers) dithia[6]radialenes on treatment with boron trifluoride etherate:[65]



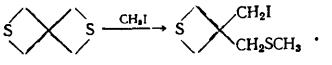
Thiiran as well as methyl 2,2-dimethyl-, hexyl-, phenyl-, and 2,3-diphenyl-thiirans, epithiocyclohexane, and epithiocyclo-octane react with 1,2-dehydrobenzene, which is a powerful electrophile, to form phenyl vinyl sulphides in 71–90% yields:[66]



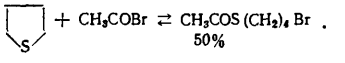
The anionic component of the intermediate betaine acts as a base and abstracts the acid hydrogen from the three-membered ring with the simultaneous formation of a C–C bond and the dissociation of the C–S bond. The reaction is stereospecific: *cis*- and *trans*-phenylthiostilbenes are formed from *cis- and trans*-2,3-diphenylthiirans respectively.

Trifluoromethylthiiran is attacked by electrophiles (Cl_2, HCL, CH_3COCl) at the sulphur atom. The products are respectively 3-chloro-1,1,1-trifluoropropane-2-sulphonyl chloride (yield 72%), 3-chloro-1,1,1-trifluoropropane-2-thiol (yield 69%), and its acetate (yield 38%).[49]

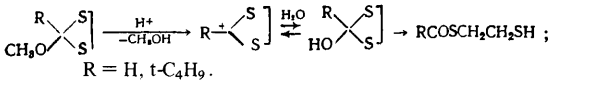
The dithiaspiroheptane ring is opened by methyl iodide:[67]



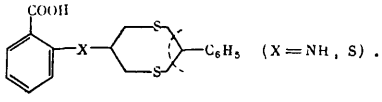
Thiolan is cleaved reversibly by acetyl bromide on refluxing:[68]



The kinetics and mechanism of the hydrolysis of 2-methoxy-1,3-dithiolans in acid media have been investigated.[69] The reaction proceeds in three stages and leads to 2-mercaptoethyl thiocarboxylates:



On treatment with mercury(II) chloride, derivatives, of 2-phenyl-1,3-dithiane split off the C_6H_5CH fragment and are converted into the mercaptides of 2-substituted propane-1,3-dithiols:[36]



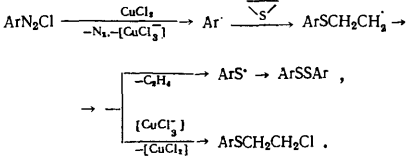
On treatment with chlorine, 2,4,6-trichloro-1,3,5-trithiane is cleaved, affording $CHCl_2-S-CHCl_2$ and $CHCl_2SCl$.[70]

3. Radical Reactions

Episulphides are rapidly desulphurised on heating with *NN*-bis-(trimethylsilyl)aminodimethylphosphine and are converted in a quantitative yield into the corresponding alkenes and the phosphine sulphide.[71] Here there is a possibility of the homolytic cleavage of the heterobond:[2]

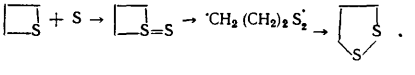


The homolytic cleavage of thiiran takes place on treatment with arenediazonium chlorides in the presence of $CuCl_2$:[72]



The reaction of thiiran with toluene-*p*-diazonium chloride afforded[72] β-chloroethyl *p*-tolyl sulphide in 50% yield relative to the *p*-toluidine employed.

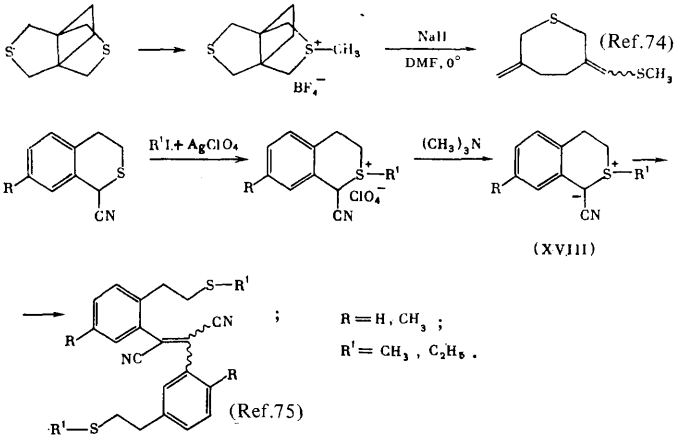
Metastable sulphur is obtained by the photolysis of gaseous COS. Under these conditions, the reaction involving thietan yields 1,2-dithiolan and ethylene in comparable amounmts as the main products.[73] The proposed mechanism of the formation of 1,2-dithiolan is as follows:



V. REARRANGEMENTS WITH CHANGE IN THE NUMBER OF MEMBERS IN THE RING

In recent years, studies on the sigmatropic rearrangements of sulphides, especially semiaromatic sulphides,‡ have been carried out widely. Such rearrangements frequently lead to a change in the number of members in the ring or to the opening of the latter[74,75] (see, for example, Scheme 1).

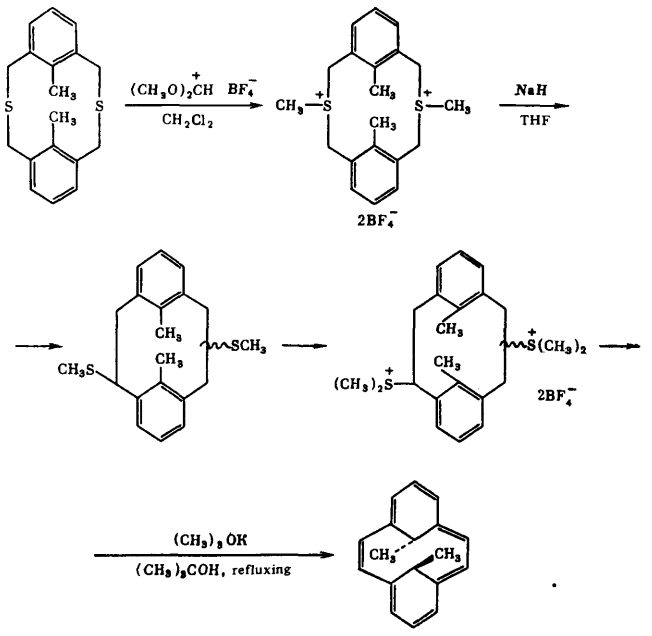
Scheme 1



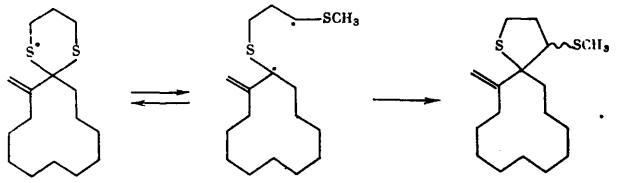
The Stevens rearrangement involves reactions of sulphonium ylides—the cyclic sulphide is initially converted into the sulphonium salt and is then acted upon by a strong base, whereupon an acyclic sulphide linkage is produced. The Stevens rearrangement is frequently used in the synthesis of cyclophanes; with its aid, a cyclic

‡ "Semiaromatic sulphides" are polycyclic sulphides where at least one carbon atom involved solely in a σ-bond, is linked to the sulphur atom.

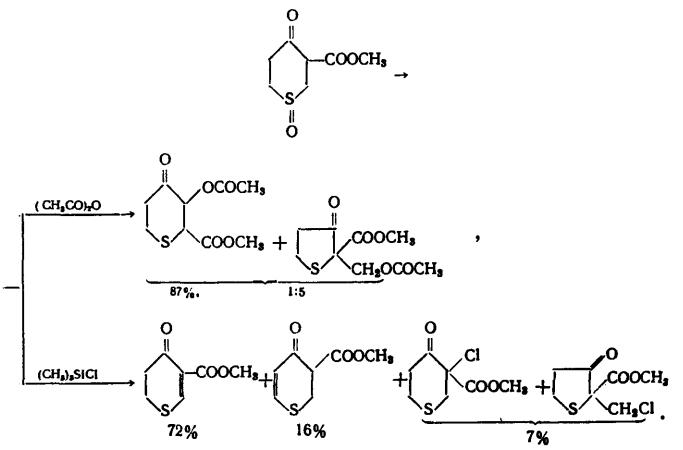
sulphide linkage is replaced (in several steps) by the C=C double bond.[76-78] A convenient methylating agent for the synthesis of the sulphonium salts is dimethoxycarbonium fluoroborate:[76]



The Stevens rearrangement can also lead to the contraction of the heterocycle:[79]

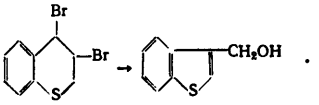


The ring contraction in cyclic sulphides can occur under the conditions of various reactions. Thus the contraction of the six-membered ring is observed on electron impact mass-spectrometry[80] and in the Pummerer rearrangement—both under standard conditions (when the sulphoxide is treated with acetic anhydride) and on reaction with chlorotrimethylsilane:[81]

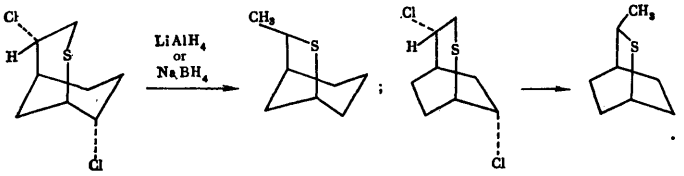


Thiane isomerises to 2-methylthiolan in the temperature range 250–350 °C in the presence of acid catalysts, among which Al_2O_3 is the most selective.[82] Thiane and thiacycloheptane initially isomerise over charcoal treated with nitric acid at 400–500 °C, producing respectively 2-methyl- and 2-ethyl-thiolans, which are then dehydrogenated (via an ionic mechanism) with the preferential formation of thiophens.[83]

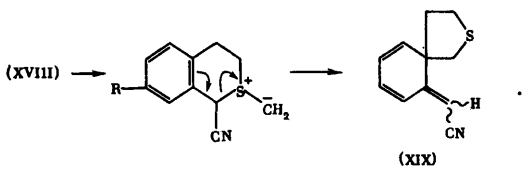
The hydrolysis of bromothiachromans and bromodihydronaphthothiopyrans in aqueous acetone with added potassium hydroxide gives rise to benzo- and naphtho-thiophens respectively,[84] for example:



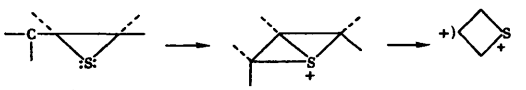
The reductive dechlorination of the adducts of 4-vinylcyclohexene with sulphur dichloride (dichlorothiabicycloalkanes) is accompanied by skeletal rearrangements—redistribution of the carbon bonds between the rings or the contraction of the heterocycle:[85]



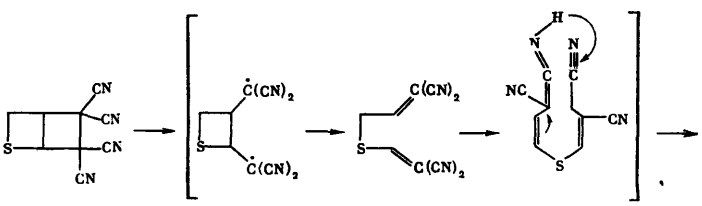
The ylides (XVIII), R′ = CH_3 isomerise in protic solvents (ethanol, methanol) with ring contraction and the formation of the spiro-compound (XIX)[75]—there is initial isomerisation to a methylide, which then undergoes a [2,3]sigmatropic rearrangement (despite the breakdown of aromaticity):

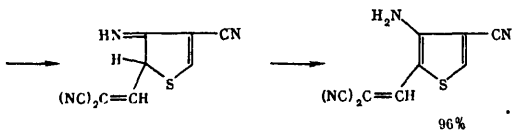


The expansion of the thiiran ring is observed in reactions of epithiohalogenohydrins with nucleophiles.[2] This involves a thiiran–thietan rearrangement. The mechanism includes a cationotropic transformation:

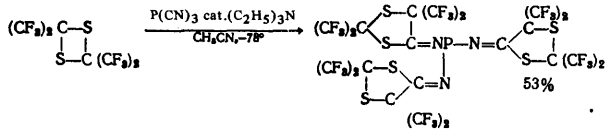


When a solution of 5,5,6,6-tetracyano-2-thiabicyclo[2.2.0]hexane in benzene is refluxed, an arrangement takes place with expansion of the thietan ring and the formation of 3-amino-4-cytano-2-(2,2-dicyanovinyl)thiophen.[86] A radical mechanism involving the opening of both rings with subsequent ring expansion in the acyclic intermediate to form iminodihydrothiophen and tautomerisation of the latter has been proposed:[86]

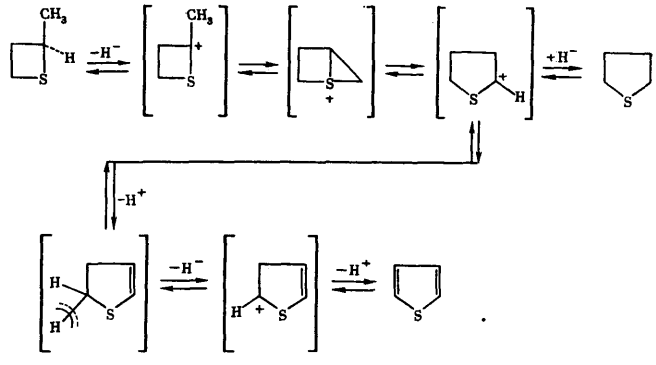




In the interaction of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan with $P(CN)_3$ or $As(CN)_3$, the latter react in the isonitrile form, a carbon atom is "inserted" in the dithiethan rings, and 1,3-dithiolan derivatives are formed:[87]

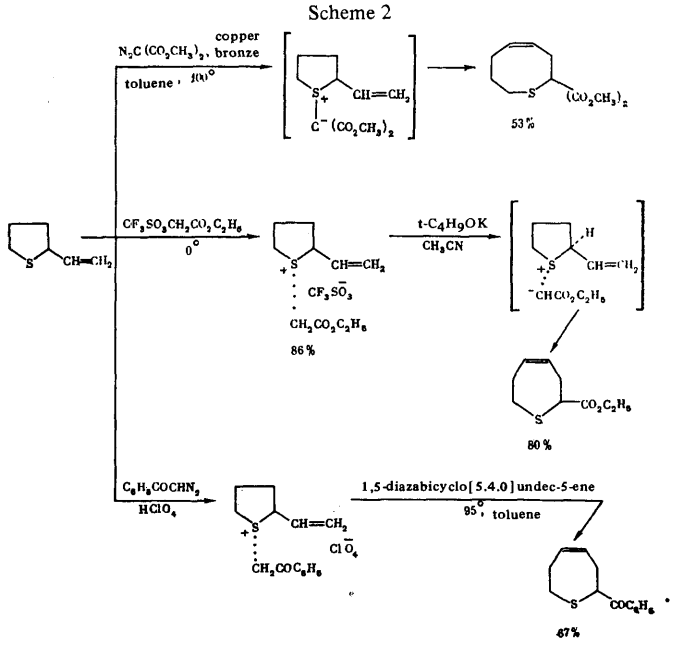


2-Methylthietan isomerises to thiolane on treatment with hydride ion acceptors—triphenylmethyl fluoroborate, chloranil, chlorotriphenylmethane—in the presence of $SnCl_4$,[88] whereupon a thiophen is also formed:



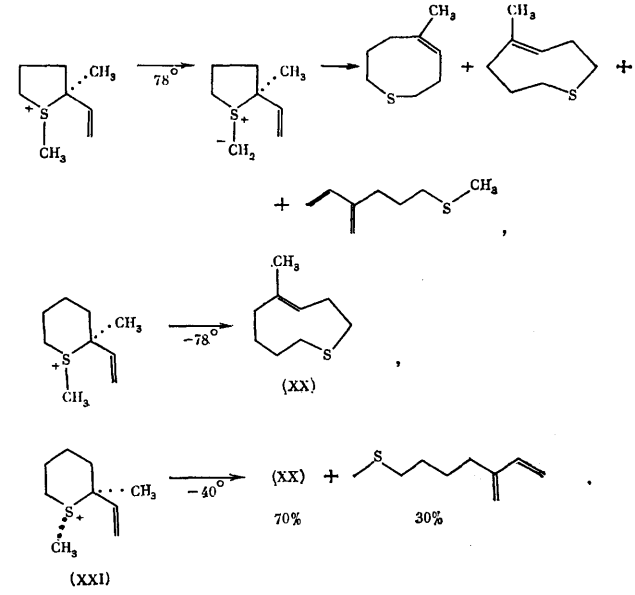
Thiacyclo-octane derivatives are obtained from vinylthiolan. The reaction is of the type of a [2,3]sigmatropic shift and proceeds via an ylide formation stage[89] (see Scheme 2).

Scheme 2

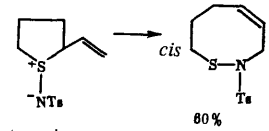


An analogous [2,3]sigmatropic ring expansion has been investigated for the salts of various 2-vinylthiacycloalkanes.[79,90-93] It has been noted that reactions involving 1,2-dimethyl-2-vinyl-substituted thiolanium and thianium hexafluorophosphates (on treatment with potassium t-butoxide) are stereoselective but not stereospecific[90] (see Scheme 3).

Scheme 3

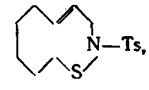


The reaction involving the stereoisomer (XXI) does not take place at −78 °C. The stereochemistry of the ring expansion in the [3,2]sigmatropic rearrangements of sulphonium ylides can depend on the way in which the ylides are formed and on the initial sulphonium salt.[91] On heating *N*-(toluene-*p*-sulphonylimino)-derivatives of 2-vinylthiolan and 2-vinylthiane in xylene, the ring expansion also takes place as a result of the insertion of the nitrogen atom:[92]



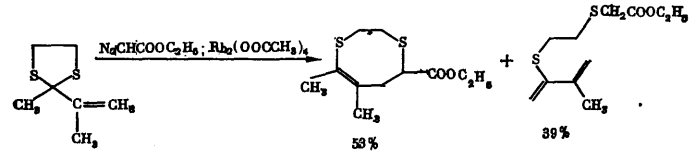
diostereoisomers

It has been suggested[91] that initially there is pyramidal inversion to the *cis*-diastereoisomer, which then rearranges. On treatment with chloramine-T in methanol at room temperature, 2-vinylthiacycloheptane immediately affords the product of the rearrangement

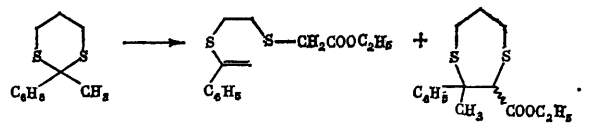


which has the *trans*-configuration.[92]

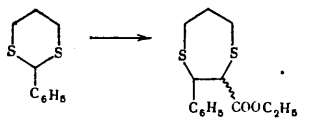
The rearrangement of 2-vinyl-1,3-dithiolans and 2-vinyl-1,3-dithianes was carried out by treatment with diazoacetic ester and rhodium tetra-acetate (the catalyst of the formation of ylides[93]) or copper sulphate,[79] for example:



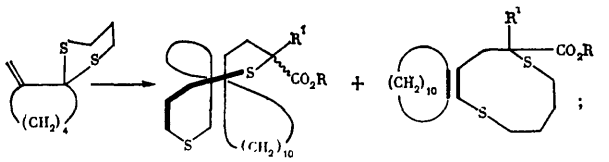
In the reaction involving 2-phenyl-1,3-dithianes under the same conditions, a [1,2]sigmatropic rearrangement takes place:[93]



The diastereoisomer ratio for the insertion product is 15, the isomer where the phenyl and ethoxycarbonyl groups are in the *trans*-positions predominating:

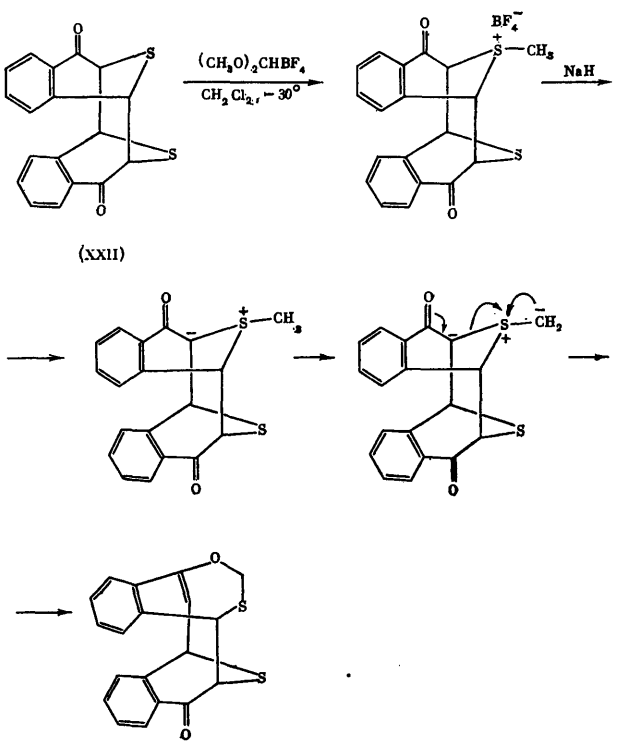


"Betweenanes" have been synthesised using ethyl diazoacetate or diazomalonate via a [2,3]sigmatropic rearrangement:[79]



$R=C_2H_5$, $R^1=H$; $R=CH_3$, $R^1=CO_2CH_3$.

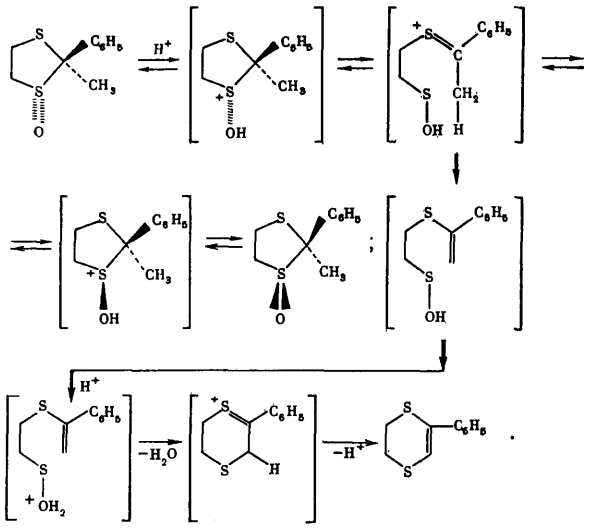
In the [2,3]sigmatropic rearrangement of the "semiaromatic" bis-sulphide (XXII), ring expansion occurred as a result of the incorporation of an oxygen atom:[94]



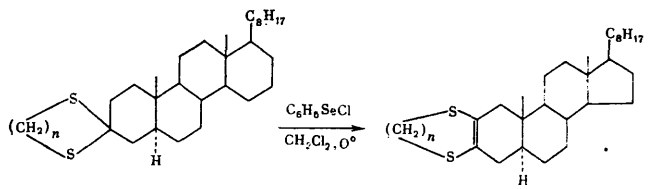
(XXII)

On heating, 2,5-di(chloromethyl)thiolan isomerises irreversibly to 2-chloromethyl-5-chlorothiane and an analogous isomerisation has been observed on heating an aqueous acetone solution of 2,5-di-(hydroxymethyl)thiolan and also on oxidation of 2,5-di(chloro-methyl)thiolan with t-butyl hydroperoxide in the presence of $MoCl_5$.[31]

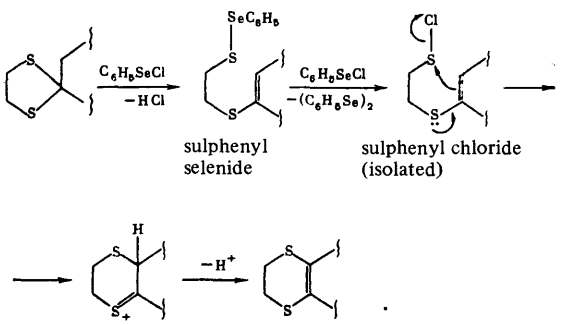
Both *cis*- and *trans*-2-methyl-2-phenyl-1,3-dithiolan monoxides are converted in a quantitative yield into 2-phenyl-1,4-dithiacyclohexene on treatment with acetic anhydride of toluene-*p*-sulphonic acid.[95] The ring expansion reaction is non-stereospecific. On initial protonation with toluene-*p*-sulphonic acid or on acylation with acetic anhydride, intermediate sulphonium ions are formed and then the C–S bond in the sulphoxide is broken and a carbosulphonium intermediate is produced, which then loses a proton; the subsequent ring closure is acid catalysed:



The expansion of the rings of 1,3-dithiolans and 1,3-dithianes takes place on treatment with benzeneselenyl chloride.[96] This reaction has been used to synthesise steroid dihydro-1,4-dithiines and dihydro-1,4-dithiepins:



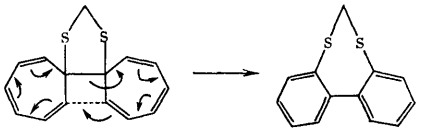
The reaction proceeds with participation of a cationic intermediate:



sulphenyl selenide

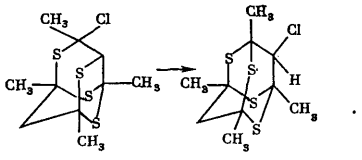
sulphenyl chloride (isolated)

The dispirodithiolan (XXIII) slowly rearranges at room temperature;[97] under these conditions, 14 electrons participate in the orbital symmetry-allowed [7,7]sigmatropic shift:

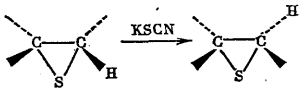


(XXIII)

On treatment with HCl in ether and on storage, the tetrathiahomoadamantane derivative (XXIV) undergoes skeletal isomerisation with expansion of one of the rings, the contraction of the other, and the formation of a tetrathia-adamantane derivative:[32]



Isomerisation without change in the skeleton, namely the epimerisation of episulphides, occurs on treatment with potassium thiocyanate in aqueous solution on heating:[98,99]



The yields in such stereoisomerisation are 10–30% for 5α,6α-epithiopregnanolone.[98] The interconversions of the *cis*- and *trans*-isomers of 3-hydroxy-1,2-epithiocyclohexanol are observed under these conditions; 3-acetoxy-1,2-epithiocyclohexanol isomerises analogously.[99]

The five- and six-membered cyclic sulphonium salts with a methyl substituent in the ring racemise on heating or, in a special case, undergo epimerisation, which apparently proceeds via the pyramidal inversion at the sulphur atom.[100] On treatment with butyl-lithium in tetrahydrofuran, 2α-phenyl-*cis*-1-thiadecalin 1,1-dioxide isomerises to 2β-phenyl-*trans*-1-thiadecalin 1,1-dioxide.[101] The inversion of the configuration on metallation involves the C(2) and C(9) atoms. During deuterium exchange, the configuration at C(2) in the initial 2α-phenyl-*cis*-sulphone is inverted and [2-D]-2β-phenyl-*cis*-1-thiadecalin 1,1-dioxide is formed.[101]

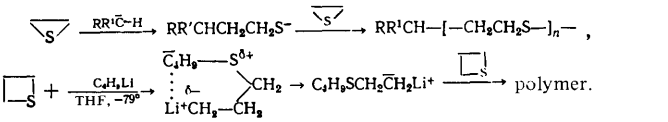
2-Methylthiaindan isomerises over $ZnCl_2/Al_2O_3$ to 3-methylthiaindan to the extent of 20%; the process may proceed with participation of a carbonium ion.[102]

VI. POLYMERISATION OF CYCLIC SULPHIDES

During the 1960's and especially 1970's, the polymerisation of thiirans and thietans became the subject of numerous investigations (see the relevant reviews[2,103,104]). Practical applications were proposed for a number of thiiran and thietan polymers and copolymers (see, for example, the patent literature in the book of Fokin and Kolomiets[2]).

In order to polymerise thiolans and thianes, the latter are initially converted into sulphonium salts (see below).

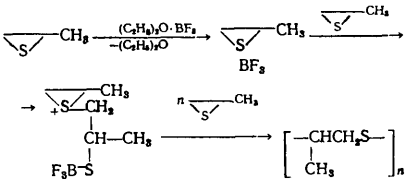
In the anionic polymerisation of cyclic sulphides, the primary condensation product has more pronounced nucleophilic properties than the initial nucleophile,[2,104] for example:



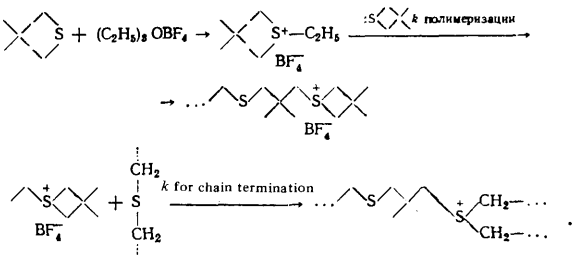
A wide variety of initiators, for example ethyl-lithium, lithium ethanethiolate, 1,4-dilithio-1,1,4,4-tetraphenylbutane,[105] and the potassium salts of aromatic nitriles and ketones[106] are used in the anionic polymerisation of thiirans and thietans. The same initiators are used in the synthesis of block copolymers of dienes with thiirans and thietans.[107,108]

4-Amino-1,2-dithiolane polymerises on heating in chloroform solution.[109]

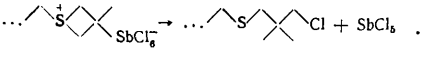
The cationic polymerisation of thiirans and thietans is usually initiated by onium compounds and proceeds via the formation of a zwitter-ion:[104]



Triethyloxonium fluoroborate[110–114] as well as 1-ethyl-3,3-dimethylthietanium fluoroborate,[110] triethyloxonium hexachloroantimonate,[115] triethyloxonium hexafluorophosphate, perchloric acid, and methyl fluorosulphonate[116] are used as catalysts of the polymerisation of thiirans and thietans. The kinetics and mechanism of the cationic polymerisation of thietans are similar to those described above[114]— chain propagation takes place as a consequence of the nucleophilic attack by the monomer directed to the α-carbon atom of the cyclic sulphonium ion. Polymerisation stops as a consequence of the reaction between the reactive chain end and the sulphur atom in the chain already formed, whereupon an unstrained sulphonium ion incapable of reinitiating the polymerisation is produced:



On initiation with the aid of $(C_2H_5)_3OSbCl_6$, chain termination is facilitated by the fact that the growing chain interacts with the counterion, forming an alkyl chloride:[115]

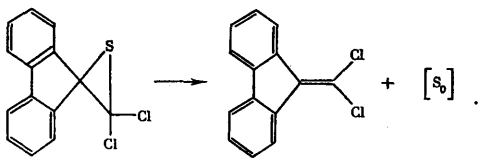


On treatment with hydrochloride, sulphuric, and phosphoric acids, 2-(*N*-carbazolyl)thiiran is converted into oligomers; the interaction with adipic, sebacic, or phthalic acid results in the formation of oligoesters, which are promising as film forming materials for the non-silver recording of information.[117]

VII. THERMOLYSIS AND FRAGMENTATION OF CYCLIC SULPHIDES

A profound change in the carbon skeleton of thiacycloalkanes can occur during their thermolysis and also under the conditions of mass spectrometry (fragmentation under electron impact; the influence of the heating of the specimen cannot be ruled out either).

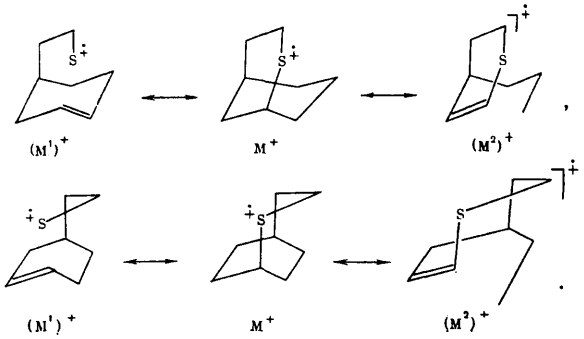
On pyrolysis, thiiran is converted into ethylenethiol and thiophen.[118] The thermolysis of the spirothiiran (XXV) leads to the formation of an olefin as a result of a complex (hitherto not ultimately elucidated) chain of reactions—the reaction order is other than first:[119]



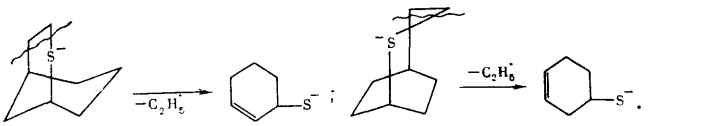
(XXV)

Mass-spectrometric study of alkyl-substituted thiolans and thianes showed[120] that the stability of the molecular ions of β-alkylthiolans is greater than for their α-isomers and that the main process in the decomposition of α-alkylthiolans is the ejection of alkyl radicals as a whole from the molecular ions. In the case of β-alkylthiolans, the main decomposition pathway involves the elimination of only part of the alkyl substituent with retention of one CH_2 group in the charged thiolanium fragment. In α- and β-thianes, the alkyl substituent is eliminated predominantly as a whole, while γ-alkylthianes behave similarly to β-alkylthiolans. The same has been observed for 4-alkyl-2-methylthianes,[121] for which, in addition, the CH_3 group is more readily split-off from the *trans*-isomers, i.e. the latter are less stable in relation to electron impact than the *cis*-isomers. In the *cis*- and *trans*-isomers of 2(4′-alkoxycarbonylbutyl-3-hydroxy-4-ureidothiolans, the splitting-off of the substituents in 3- and 4-positions under electron impact also takes place with different degrees of ease, which makes it possible to identify the geometrical structure.[122]

A combination of positive and negative ion mass spectrometry has been used to establish the structures of bridged thiabicyclooctanes and thiabicyclononanes, including methyl-substituted compounds.[12] The characteristic features of the fragmentation of the positive ions M^+ exist in the transition state $(M^1)^+$,$(M^2)^+$:



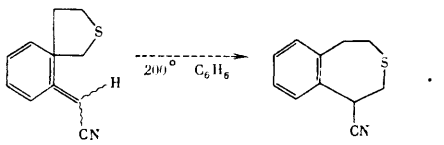
The decomposition of molecular negative ions involves the rupture of the C—C bonds (at the junction) and C—S bonds with localisation of the negative charge on the sulphur atom:



The characteristic feature of the decomposition of negative ions made it possible to infer unambiguously the presence of substituents at the α-carbon atom (relative to the sulphur atom).

The fragmentation of 1,3-dithiolan under electron impact has been examined[124] and the heat of formation of the free radical CHS˙, amounting to 63 kcal mol^{-1}, has been obtained from the appearance potentials of the $[C_2H_5S]^+$ ion.

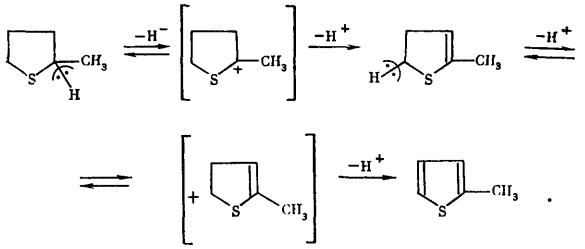
When the spiran (XIX) is heated in benzene (in a sealed tube), thermal isomerisation takes place with formation of a seven-membered ring:[75]



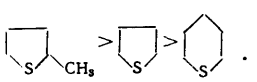
(XIX) 82%

VIII. DEHYDROGENATION AND DESULPHURISATION OF CYCLIC SULPHIDES

Thiolan, 2-methylthiolan, and 2-methylthiaindan are dehydrogenated to the corresponding thiophene derivatives in the presence of acid catalysts—$ZnCl_2/Al_2O_3$ and aluminosilicate;[82,125] the process takes place on aprotic catalyst centres and includes stages in which hydride ions are abstracted and cationic intermediates are formed:

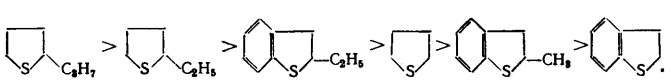


2-Methylthiolan is dehydrogenated more readily than the unsubstituted compound, owing to the greater hydride mobility of the hydrogen atom. It decreases in the sequence[126]



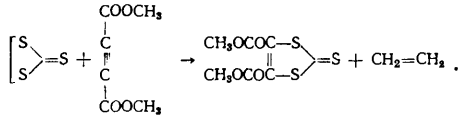
Using cyclic sulphides as hydride ion donors in the ionic reduction of carbonium ions, it is possible to obtain their dehydrogenation products: 2-methylthiophen from thiane (the reaction is accompanied by isomerisation)[127] and 2-methylthiaindene from 2-methylthiaindan in 87% yield (according to gas—liquid chromatographic data).[128]

The rate constants for the dehydrogenation of cyclic sulphides in the presence of activated charcoals at 400 °C decrease in the sequence[129]

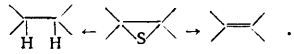


It is appropriate to mention that, according to the EPR spectra of the free radicals formed as a result of the abstraction of hydrogen, the protons in the α-position relative to the sulphur atom in thiolan, thiane, and 4-t-butylthiane are not equivalent.[130]

An unsaturated heterocycle can be obtained from a saturated hetearocycle not only on dehydrogenation but also in an exchange reaction:[131]

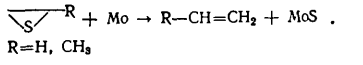


The hydrodesulphurisation of thiirans leads to alkanes; sometimes the reaction stops at the formation of olefins:

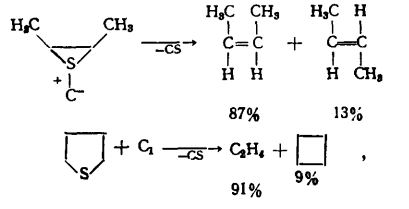


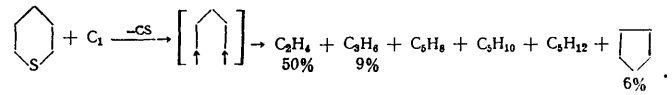
Various hydrodesulphurisation methods have been investigated[132] for the alkylthiirans: dodecylthiiran, 2-methyl-2-nonylthiiran, 2,3-dioctylthiiran, and 3-decyl-2,2-dimethylthiiran. In the presence of Raney nickel of lithium, monosubstituted 2,3-disubstituted thiirans react with ethylamine at a low temperature, giving rise to alkanes. The desulphurisation of tri- and tetra-substituted thiirans stops at the formation of alkenes. On treatment with zinc in acetic acid or with tributyltin tetrahydroborate, only olefins are formed, the reaction being regioselective but not fully stereoselective. The reduction with P_2I_4 in dimethylformamide (DMF) is highly stereoselective and leads to olefins having the same configuration as the initial thiiran. However, the first two methods can also be used to synthesise olefins if the reaction is carried out with heating. The yields are high in all the methods.

When cyclic sulphides are treated with metallic molybdenum, the degree of desulphurisation diminishes with decrease in ring strain.[133] The reaction of thiiran and 2-methylthiiran afforded the corresponding alkenes in 132 and 119% yields relative to the evaporated molybdenum:

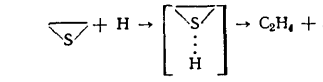


Propene and a small amount of cyclopropane are formed from thietan. It has been suggested that either a biradical is formed as a result of the simultaneous rupture of both C–S bonds or the reaction proceeds with participation of a π-allyl intermediate. The addition of tetraethylthiiran disulphide increases the yield of propene to 77%. The reaction of thiolan results in the formation mainly of hydrogen and a complex mixture of C_1-C_4 products, including 15% of butanethiol. When a cyclic sulphide interacts with carbon vapour (produced from carbon electrodes in a voltaic arc), desulphurisation takes place.[134] The process proceeds via an intermediate ylide, formed when the electrophilic carbon atom and the free electron pair of the suphur atom interact. A CS polymer is formed as a result of the decomposition of the ylide:

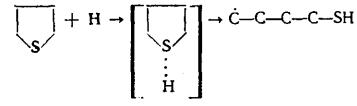




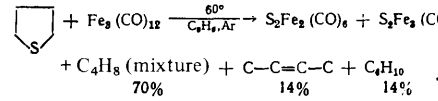
When thiiran is reduced with hydrogen under pressure,[135] ethylene is formed, the sulphur atom being eliminated in the form of a univalent radical:



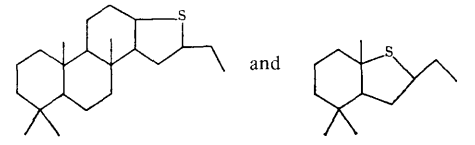
In the reaction involving thiolan, the formation of a mercaptobutyl radical is most probable and in this case the C–S bond is broken:[135]



In the desulphurisation of thiolan by treatment with triiron dodecacarbonyl, the reaction proceeds via a stage involving metal carbonyl sulphide clusters:[136]



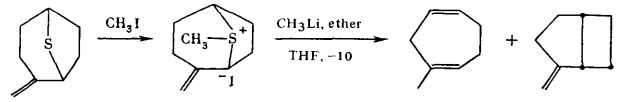
The hydrodesulphurisation of polymethylthiolans and polymethylthianes on the AP-56 industrial platinum catalyst at 350 °C takes place without the decomposition of the carbon skeleton and can be used to investigate petroleum sulphides present in the petrol fractions.[137] Despite the fact that the hydrodesulphurisation over Raney nickel can induce rearrangements and condensation reactions,[1] this reaction has been used to establish the structure in the synthesis of thiabicycloalkanes.[138] The structure of the bicyclic and tetracyclic terpenoid sulphides[139] of the type



found in Athabasca bitumen (a petroleum deposit in Virginia, USA) has also been established with its aid.

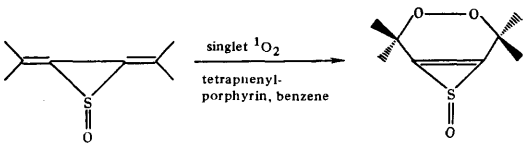
In the synthesis of gramicidin, the desulphurisation of 1,3-dithianes takes place on treatment with lead dioxide and boron trifluoride in methanol[37] (see above).

Sulphur is split-off on treatment of methylsulphonium salts [or their precursors?], for example, 2-methylene-8-thiabicyclo[3.2.1]-octane, with methyl-lithium;[140] for the removal of the sulphur atom, it is essential that at least one of the carbon atoms at the junction should be of the benzyl or allyl type:



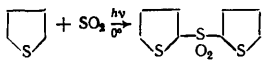
IX. PHOTOCHEMICAL REACTIONS OF THE SULPHIDES

There have been few studies on the photochemical reactions of saturated cyclic sulphurides. The photochemical oxidation of thiiranoradialene sulphoxide (XXVI) leads to thiirene sulphoxide (XXVII) joined to an *endo*-peroxide ring:[141]



(XXVI) (XXVII), 72%

Thiolan combines with sulphur dioxide on irradiation with UV light:[142]



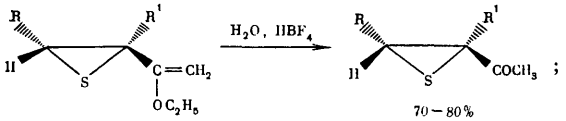
The methylenation of thietans, thiolans, and thianes with the aid of diazomethane on irradiation with UV light leads to alkylthiacycloalkanes;[143] the reaction has been used to identify cyclic sulphides by gas–liquid chromatography.

The decomposition of polycyclic "semi-aromatic" sulphides by light results in the formation of cyclophanes.[144]

X. INTRODUCTION OF FUNCTIONAL GROUPS WITHOUT CHANGE IN THE CARBON SKELETON

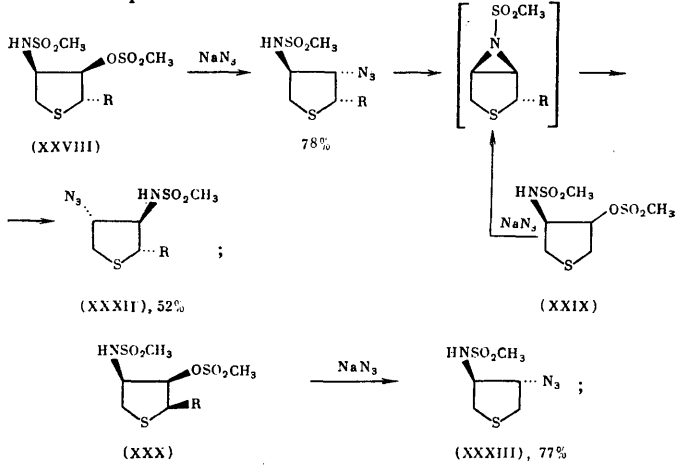
The stereochemical aspect of the study is of special interest in reactions involving the introduction of a functional group.

When ethoxyvinylthiirans undergo acid hydrolysis to acetylthiirans, the configuration is retained:[145]



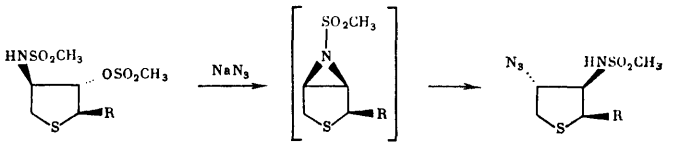
R, R¹ = H, CH_3.

The reaction of four stereoisomers of 2,3,4-trisubstituted thiolans (XXVIII)–(XXXI) with sodium azide[146] leads to the formation of only the *trans*-3,4-disubstituted compounds (XXXII)–(XXXIV). Consequently, the reaction of the *cis*-3,4-disubstituted thiirans takes place with inversion of the configuration at C(3), while the reaction of the *trans*-3,4-disubstituted compounds proceeds in an unusual manner—without change in configuration. The intermediate formation of the aziridine ring has been suggested[146] and in the case of compounds (XXVIII), (XXIX), and (XXXI) the reaction is accompanied by the migration of the substituents from the 3-position to the 4-position:



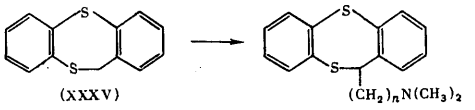
(XXVIII) (XXXII), 52% (XXIX)

(XXX) (XXXIII), 77%



(XXXI) R = $(CH_2)_4COOCH_3$ (XXXIV), 77%

The reaction of 11*H*-dibenzo[*b*,*e*]-1,4-dithiepin (XXXV) with fairly strong bases leads to the abstraction of the proton in the 11-position and the formation of the corresponding carbanion or an organometallic compound.[147] The reaction of the organolithium compound obtained in this way with 2-dimethylaminoethyl chloride or with 2-dimethylaminopropyl chloride affords compounds (XXXVI) or (XXXVII) (isolated in the form of acid oxalates), which exhibit an antireserpine activity:

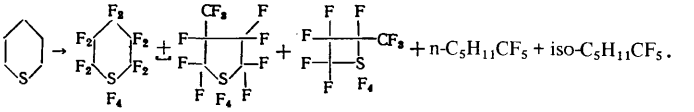


(XXXV) (XXXVI) n = 2 (XXXVII) n = 3

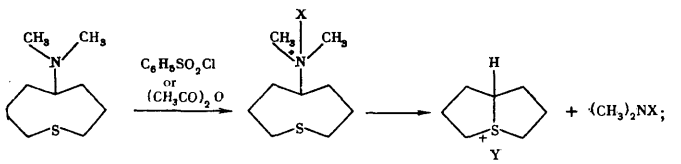
The cyanoethylation of methyl-4-thianones proceeds in different ways depending on the position of the substituent.[148] 2-Methyl-4-thianone gives rise to only 5-(2-cyanoethyl)-2-methyl-4-thianone, 2,2-dimethyl-4-thianone affords only 5,5-di(2-cyanoethyl-2,2-dimethyl-4-thianone, while 3-methyl-4-thianone gives rise to both 3-(2-cyanoethyl)-3-methyl-4-thianone and 3,5-di(2-cyanoethyl)-3-methyl-4-thianone. The authors[148] explain this by the different influences of the substituent on the conformation of the intermediate carbanions.

On treatment with *N*-chlorosuccinimide in benzene (at 20–25 °C), thiolan, thiane, and thiepan produce the corresponding α-chlorothiacycloalkanes.[149]

The electrochemical fluorination of thiolan, 2-methylthiolan, and thiane in anhydrous HF at 5–6 °C [150] involves complete fluorination, for example:

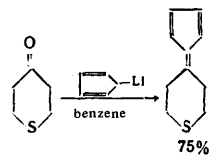


The unusual "functional group elimination" reaction occurring in the interaction of 5-(dimethylamino)-1-thiacyclo-octane with benzenesulphonyl chloride[151] leads to 1-thioniabicyclo[3.3.0]octane benzenesulphonate (compounds of this type are called Eastman's salts) and *NN*-dimethylbenzenesulphonamide in nearly quantitative yields. Acetic anhydride behaves analogously:

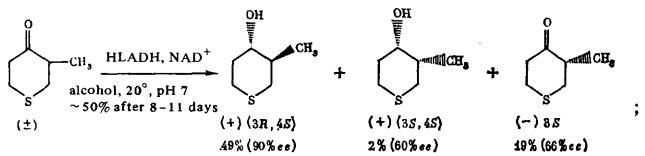


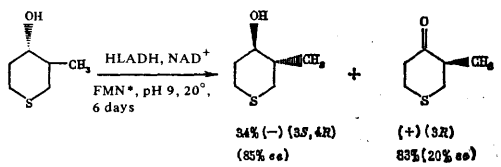
X = $C_6H_5SO_2$ or CH_3CO;
Y = $C_6H_5SO_2O^-$ or CH_3COO^-.

The reactions of the keto-group in thiacycloalkanes are used for synthetic purposes; for example, lithiocyclopentadiene reacts with 4-thianone:[152]



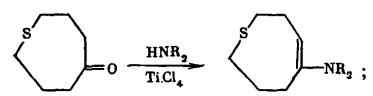
The enzymatic reduction of the keto-group in 4-thianones by horse liver alcohol dehydrogenase (HLADH) in the presence of a co-enzyme—a nicotinamide derivative (NAD^+)—proceeds with high stereoselectivity and enantiomeric selectivity.[153] The oxidation of *trans*-4-thianols with participation of HLADH is also promising for the synthesis of enantiomers which have not reacted (the *cis*-isomers are oxidised very slowly):[143]





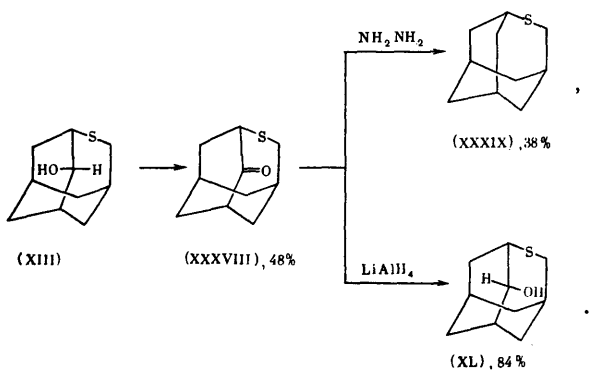
*FMN = flavin mononucleotide (recyclising agent).

5-Thiocanone reacts with secondary amines to produce enamines—derivatives of tetrahydrothiocin:[154]



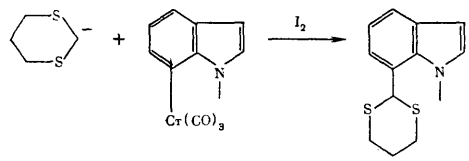
$R_2 = (CH_3)_2, -(CH_2)_4-, -(CH_2)_2-O-(CH_2)_2-$.

The reduction of 2-methyl-1-thiadecalones and 2-methyl-1-thiahydrindanones with hydrazine hydrate leads to a mixture of stereoisomeric 2-methyl-1-thiadecalins or 2-methyl-1-thiahydrindans; the stereoisomers are separated chromatographically.[155] 4-Thiahomoadamantan-2-one (XXXVIII) [obtained by oxidising compound (XIII)] is reduced[39] to 4-thiahomoadamantane (XXXIX) in the same way; the reduction of compound (XXXVIII) with lithium tetrahydroaluminate leads to a stereoisomer of 2-hydroxy-4-thiahomoadamantane (XL):



Treatment of compound (XIII) with thionyl chloride produces[39] the corresponding chloride in 98% yield; it is reduced with lithium tetrahydroaluminate to compound (XXXIX) in 82% yield.

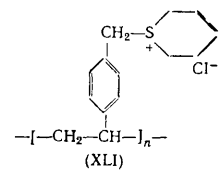
The nucleophilic attack by 2-lithio-1,3-dithiane is directed to the 7-position in π-indolechromium tricarbonyl and a 7-substituted indole is formed in a high yield;[156] the chromium π-complexes are decomposed with iodine:



XI. THE SYNTHESIS AND REACTIONS OF CYCLIC SULPHONIUM SALTS

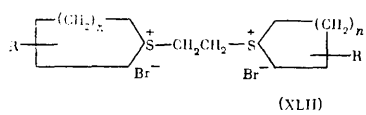
The introduction of functional groups into cyclic sulphides by converting them into sulphonium compounds is important. They are extremely promising for practical use and also open up pathways to the synthesis of a wide variety of polyfunctional compounds, especially compounds based on thioniacycloalkanes.

Chlorobenzylthiolanium and chlorobenzylthianium halides are formed when cyclic sulphides interact with chlorobenzyl halides in nitromethane (the yields of the sulphonium salts are 43–72%).[157] The vinylbenzylthianium and vinylbenzyl(3-pentyl)thiolanium halides are obtained analogously to serve as monomers for the preparation of polymers of type (XLI) by radical polymerisation; aqueous solutions of the polymers are used as flocculants:[158]



(XLI)

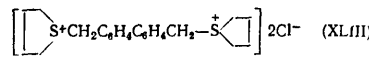
Ethylenebis-sulphonium salts of type (XLII) have been patented[159] as fungicides and agents active against phytopathogenic microbes; the salts are obtained from ethylene dihalide and a cyclic sulphide in DMF at 75 °C:



$n = 0.1$; R = Cl, Br, alkyl, alkoxyl, carboxyl

(XLII)

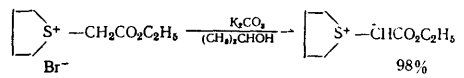
The bis-sulphonium salt (XLIII)



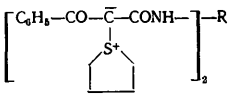
(XLIII)

was obtained[160] by heating thiolan and 4,4′-di(chloromethyl)biphenyl in concentrated hydrochloric acid at 65 °C (yield 98%). Salts of this type, including those obtained from thiane and thiepan,[160] serve as intermediates in the synthesis of dyes.

Stable ylides, for example:[161]



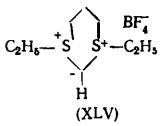
can be obtained by treating with bases thiolanium[161] or dithiolanium[162] salts having electron-accepting substituents. Ylides of types (XLIV) are used as cross-linking agents for carboxyl-containing polymers:[163]



(XLIV)

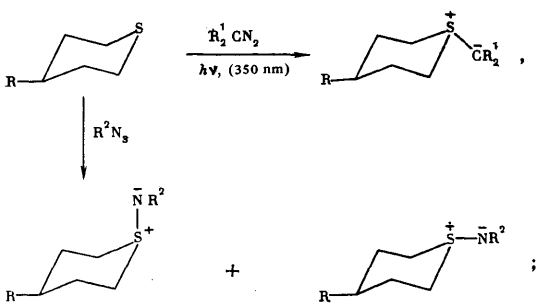
R=$C_6H_4OC_6H_4$, from C_2 to C_{20}.

Bis-sulphonium salts—alkyl-substituted 1,3-dithiolanium and 1,3-dithianium picrates and fluoroborates—are powerful CH acids:[164] 1,3-diethyl-1,3-dithianium bis(tetrafluoroborate) is deprotonated and gives rise to the stable ylide salt (XLV):



(XLV)

Only one sulphonium ylide is formed on interaction of 4-t-butylthiane with carbenes as a result of equatorial addition; on interaction with nitrenes, a 1 : 1 mixture of diastereoisomeric iminosulphuranes is formed in each case:[165]



R = t-C_4H_9, R^1 = $COCH_3$, $COOCH_3$, R^2 = *p*-CH_3-$C_6H_4SO_2$, COO_2H_5.

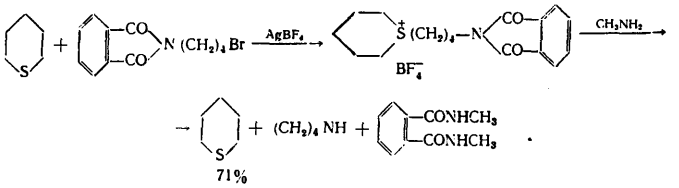
Eastman's salts—fluorides of 1-thioniabicyclo[4.4.0]decane and 6-methoxycarbonyl-1-thioniabicyclo[4.4.0]decane—have been obtained as *cis*- and *trans*-stereoisomers (isolated in the purest form) and from them ylides were synthesised:[166] the ylide from the *cis*-isomer is more stable.

Conformational analysis of the salts of methyl-substituted *cis*-1-thioniabicyclo[4.3.0]nonane derivatives has been carried out.[167]

The conformational energy of the equilibrium transition between the axial and equatorial forms of 1-methylthianium hexafluorophosphates and perchlorates, obtained by methylating thiane, 2-, 3-, and 4-methylthianes, and the *cis*- and *trans*-stereoisomers of 2,6-, 3,5-, 2,5-, and 2,4-dimethylthianes, 3,4-, 3,3-, and 4,4-dimethylthianes, 3,3,5- and 2,2,4-trimethylthianes, and 4-t-butylthiane, has been measured.[168] Its value is low for these salts (0.0 – 0.3 kcal mol^{-1}). 1-Phenyl- and benzyl-thianium and the diastereoisomeric 4-t-butyl- and 1-benzyl-2,6-dimethyl-thianium fluoroborates, 4-t-butyl-1-ethylthianium perchlorates, and 1-methyl-*cis*- and 1-methyl-*trans*-thiadecalinium hexafluorophosphates and perchlorates have been obtained by alkylating the corresponding sulphides.[168]

Thianes are deuteriated using sulphonium salts;[169] the methiodides are obtained and the acid α-hydrogen atoms are subjected to deuterium exchange (base catalysis in solution in D_2O), the sulphonium salt is reisolated, and dry-distilled to give the deuteriated thiane.

A method for protecting the sulphide sulphur against the action of metal catalysts, electrophiles, and oxidants by converting the sulphides into the 4-aminobutyl- or *p*-methoxybenzyl-sulphonium salts, which are cleaved with regeneration of the sulphides, has been proposed recently:[170]



71%

A method for the preparation of the perchlorates of 4-hydroxyarylthioniacycloalkanes by condensing thiacycloalkanes with phenols in the presence of perchloric acid, phosphoryl chloride, and hydrogen peroxide or by condensing thiacycloalkane oxides under the same conditions but without hydrogen peroxide has been put forward.[171] In the 4-hydroxy-phenylthiolanium and 4-hydroxy-1-naphthylthiolnium perchlorates obtained in this way, there is a hydrogen bond between the hydroxyls of the cation and the oxygen of the anion.[172,173] Furthermore, in 4-hydroxyphenylthianium perchlorate there is a bifurcated hydrogen bond formed by the hydroxyl of another cation and two oxygen atoms of two other anions.[174]

The perchlorates of *p*-hydroxy- and *p*-methoxy-phenylthioniacycloalkanes have been obtained from the petroleum sulphoxides and phenol and anisole.[175] The condensation of the petroleum sulphoxides with phenol then proceeds selectively—only thiamonocycloalkane oxides interact under these conditions.

4-Hydroxy-2(3)-methyl-, 2,4-dihydroxy-, 2,3,4-trihydroxy-, and 2,5-dihydroxy-phenylthiolanium chlorides have been obtained by the reaction of substituted phenols with thiolan and chlorine;[6] the yields (57 – 75%) vary in parallel with the activity of the phenols.

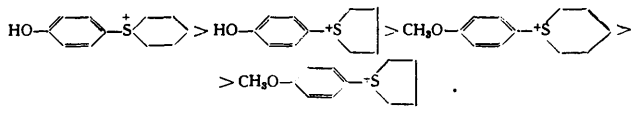
Sulphonium salts have been obtained by the interaction of thiolan with alkenes or quinones in a strong acid.[176,177] The latter method has been modified[178] and has led to a single-stage procedure for the synthesis of a wide variety of salts of 2,5-dihydroxyphenylthioniacycloalkanes in good yields (as a rule 60 – 100%). The OH group in 2,5-dihydroxyphenylthianium perchlorate, located in the 5-position in the cation, is hydrogen-bonded to the oxygen atom of the anion.[179] In the hydrate of 2,5-dihydroxyphenylthianium chloride,[178] there are three types of hydrogen bonds: between the OH group in the 2-position in the cation and the chloride anion, between the OH group in the 5-position in the cation and the oxygen atom of water, and also between a water molecule and two chloride anions.[180]

The petroleum sulphides obtained from the middle fractions of petroleum have been converted by condensation with *p*-benzoquinone and hydrochloric acid into the chlorides of 2,5-dihydroxyphenylthioniacycloalkanes (yield up to 75%).[181] Sulphonium salts—water-soluble dyes for polyester fibres—have been obtained[182] by condensing thiacycloalkanes with anthraquinones by Bosshard's method.[177]

The C – S bond dissociation reactions on treatment of arylthiolanium and arylthianium salts with nucleophiles have been investigated.[183-185] The ease of dissociation of the C – S bond varies in parallel with the degree of nucleophilicity of the reagent:[185]

$$CH_3O^- \geqslant Cl^- > Br^- > I^- \geqslant (NO_2)_2C_6H_2O^- .$$

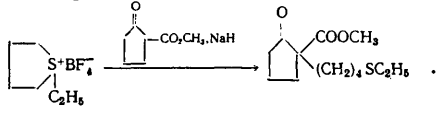
The relative stabilities of the heterocycle in the cations of sulphonium perchlorates decrease in the sequence[185]



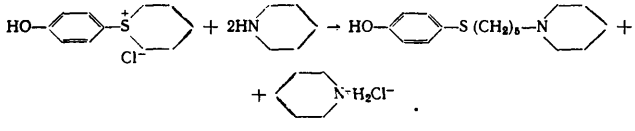
The interaction of salts of *p*-methoxyphenylthioniacycloalkanes with an aqueous or methanol solution of potassium hydroxide gives rise to ω-hydroxy-, ω-methoxy-, or ω-chloro-substituted butyl or pentyl *p*-methoxyphenyl sulphides in preparative yields (60–86%).[185]

On treatment with potassium t-butoxide in DMSO, phenylthiolanium perchlorate decomposes into phenyl vinyl sulphide and ethylene, while phenylthianium perchlorate affords 100% of the β-elimination product $C_6H_5S(CH_2)_3CH=CH_2$.[183] When these salts are treated with sodium ethoxide in alcohol, mixtures of β-elimination and α-substitution products are formed; in the case of the thianium salt, the latter predominates.[183]

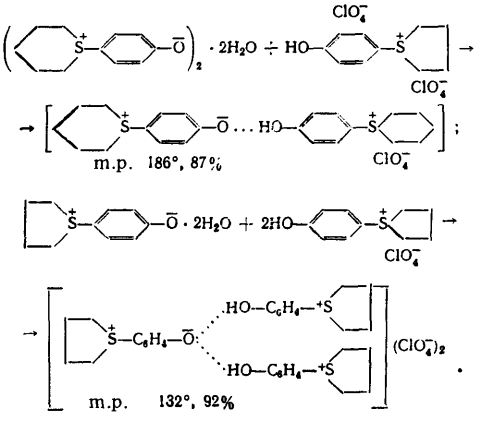
Cyclic sulphonium salts have been used for the *C*-alkylation of β-ketoesters,[186] for example:



When salts of arylthioniacycloalkanes interact with amines, the C–S bond is broken and the main amine adds on; this reaction constitutes a simple single-stage method of synthesis of ω-aminoalkyl aryl sulphides and their salts, for example:[187,188]



On treatment with bases, *p*-hydroxyphenyl-1-thiolanium and *p*-hydroxyphenyl-1-thianium salts form hydrated zwitter-ions, which readily lose water on heating and polymerise.[171,185,189–193] The zwitter-ions are also stabilised by the perchlorates of *p*-hydroxyphenylthioniacycloalkanes; stable crystalline polysulphonium salts with complex cations, formed with participation of hydrogen bonds, are then obtained:[189,190]



The oligomers produces from *p*-(1-thiolania)phenoxide with the $-[S(CH_2)_4OC_6H_6]-$ fragment have an end group with an unopened thiolanium ring; on treatment with amines, the end group is opened, affording an aminosulphide residue.[190]

Hydroxyarylthioniacycloalkane zwitter-ions are apparently polymerised via a cationic mechanism. The polymers can be used to obtain water-resistant thermoplastic resins, coatings, films, and impregnating agents.[192–195] The hydrated *p*-(1-thiolania)phenoxide and *p*-(1-thiolania)-*o*-cresolate zwitter-ions are used[196,197] as catalysts of the polycyclotrimerisation of aryl isocyanates.

The addition of *p*-t-butylthiolanium bicarbonate or bisulphate to carboxylated polymers increases the water resistance of the films obtained from them.[198]

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Transition Metal Percarboxylates, Alkylperoxides, and Hydroperoxides

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Data on methods for preparing transition metal percarboxylates, alkylperoxides, and hydroperoxides are systematically reviewed. The factors determining their stability and the most typical routes for their reactions are discussed. The ability of these compounds to act as efficient carriers of oxygen atoms to substrates of various kinds is emphasised using numerous examples.
The bibliography includes 179 references.

CONTENTS

I. Introduction 668
II. Methods of preparation 668
III. Properties 672
IV. Participation in reactions where there is stoichiometric oxidation of organic and inorganic substrates 674
V. Participation in the catalytic oxidation of organic and inorganic substrates 676

I. INTRODUCTION

The development of the chemistry of peroxide complexes of transition metals (TMPC's), such as complexes of the types $L_nM\langle^{O}_{O}|$, L_nMOOML_n, L_nMOOR (where M is a transition metal, L an organic or other ligand, and R = H, alkyl or a substituted alkyl, or R'CO), is of great importance for solving theoretical and practical problems in the catalytic oxidation of substrates of various kinds. The large amount of data so far accumulated give good reason to suppose that peroxide complexes with this structure, which are intermediates in biological oxygenation processes[1,2] and the catalytic oxidation of alkenes, alkanes, alcohols, amines, phosphines, sulphides, etc. by molecular oxygen and hydroperoxides,[3-11] are responsible for the transfer of oxygen to the oxidisable substrate, which may take place stereospecifically or stereoselectively.

The natural interest of research workers in reactions involving peroxide complexes leads to the publication in the domestic and foreign literature of an ever increasing amount of pertinent data which needs classifying. Progress in the chemistry of transition metal mono- [metal] and di-[metal]-peroxo-complexes $L_nM\langle^{O}_{O}|$ and L_nMOOML_n is comparatively fully reported in a number of reviews.[12-16] The role of the peroxides L_nMOOR (TMPC) in the mechanism of catalytic epoxidation and ketonisation of alkenes is discussed in detail in other reviews.[3-10]

There is an absence of articles of a general nature in which various aspects of the chemistry of TMPC's, such as methods of preparation, physicochemical properties, and stoichiometric and catalytic oxidation involving them, might be discussed.

The aim of the present review is to fill an existing gap in the classification of data on the chemistry of transition metal percarboxylates and alkyl- and hydro-peroxides.

II. METHODS OF PREPARATION

1. Transition Metal Alkylperoxides

Transition metal alkylperoxides are the most widespread of the TMPC's presently known.

The first peroxides of this type to be prepared were titanium compounds with the general composition $R_{4-n}Ti(OOR)_n$, which are formed by the reaction of titanium halides or alkoxides with t-butyl hydroperoxide:[17]

$$TiCl_4 + n\,Bu^tOOH \xrightarrow[NH_3\cdot py]{0\div 20^\circ C} (Bu^tOO)_nTiCl_{4-n} + n\,HCl, \quad (1)$$

$$Ti(OPr^i)_4 + n\,Bu^tOOH \xrightarrow[py]{0\div 20^\circ C} (Bu^tOO)_nTi(OPr^i)_{4-n} + n\,Pr^iOH. \quad (2)$$

This method[17] for preparing TMPC's, the basis of which is substitution of one of the ligands attached to the metal (usually a halide, hydroxide, or alkoxide):

$$L_nMX + ROOH \rightarrow L_nMOOR + HX \quad (3)$$

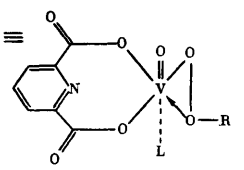
has also been used to prepare alkylperoxides of titanium (X = acac, OEt; $R = Bu^t$),[7,18-20] vanadium ($X = OEt, OPr^i, OBu^t$, $R = Bu^t$),[21-26] and palladium and platinum (X = an anion of a carboxylic or sulphonic acid; R = alkyl, aryl, or arylalkyl;[27-30] or X = OH; $R = Bu^t$ [31,32]).

If X in the complex L_nMX in Eqn.(3) is a halogen or a carboxylate anion, in place of ROOH the alkali metal salts can be used. The alkylperoxides of palladium, platinum,zirconium, and rhodium have been obtained in this way.[30,33-35]

The preparations[3] of the alkylperoxides of the vanadium dipicolinates (dipic)V(O)(OOR)L [L = H_2O or HMPT (hexametapol); R = Bu^t, cumyl],[36,37] which are described by Eqns.(4) and (5):

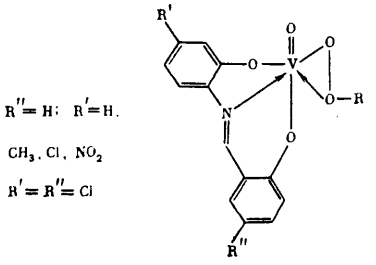
$$V_2O_5 + \text{dipic}\,H_2 + ROOH \xrightarrow{H_2O} \text{(dipic)}\,V(O)(OOR)\cdot H_2O \quad (4)$$

$$V(O)(OPr^i)_3 + HMPT + \text{dipic}\,H_2 + ROOH \rightarrow \text{(dipic)}V(O)(OOR).HMPT + 3Pr^iOH \quad (5)$$

(dipic)V(O)(OOR)·L ≡ 

are variations on Eqn.(3).

Alkylperoxides of oxo-[*N*-(2-oxidophenyl)salicylideneiminato]-vanadium have been obtained in a similar way:[38]

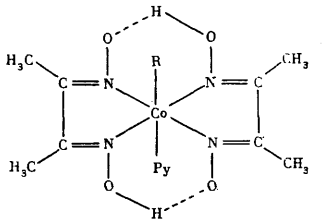


Reactions (4) and (5) have been shown to proceed via the complexes (dipic)V(O)OH.H_2O and (dipic)V(O)(OPr^i).HMPT respectively, which react with ROOH to form the desired products.

The replacement of the ligands attached to the metal by the alkylperoxide moiety can be initiated by ultraviolet light, as in the reaction of alkylpyridinecobaltoximes R[Co]py with R'OOH:[39]

$$R\text{-}[Co]\text{-}py + 2R'OOH \xrightarrow[C_6H_6/N_2]{h\nu} py[Co]OOR' + R'OOR, \quad (6)$$

where R = cumyl or t-butyl, and R' = $C(CH_3)_3$, $C(CH_3)_2C_6H_5$, $CH(CH_3)C_6H_5$, C_6H_{11}, or $CH(CH_3)C_6H_4CH_3$, and [Co] represents a Co^{II} oxime or $(Dmg)_2Co$.



This last process[39] takes place via a stage in which there is photodissociation of the metal–carbon bond and the (py)Co^{II} complex formed then reacts with ROOH.

Another general method for the preparation of transition metal alkylperoxides is based on the attachment of ROOH or the peroxide moiety OOR to transition metal complexes (TMC's), which may take place with or without a change in the oxidation state of the metal:

$$L_nM + ROOH \longrightarrow L_nM^{+}\bar{O}OR \quad (7a)$$

$$L_nM + ROOH \longrightarrow L_nM^{2+}(\bar{O}OR)(H^-) \quad (7b)$$

$$L_nM + RO_2^{\cdot} \rightarrow L_nM^{+}\bar{O}OR \quad (8)$$

$$L_nM{=}O + ROOH \rightarrow L_nM\begin{matrix}OOR\\OH\end{matrix} \quad (9)$$

Reaction(7)† has been carried out in the following cases:

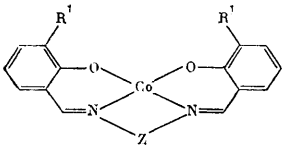
(1) For $(Arene)_2Cr$ complexes and molybdenum and tungsten cyclopentadienyl complexes Cp_2MX_2 (X = Cl, Br, I), giving the peroxides $Ar_2Cr^{+}(OOR.ROOH)^{-}$ (R = Bu^t, cumyl)[40] and $Cp_2MX_2^{+}(OOR.ROOH)^{-}$ (R = t-butyl, cumyl, t-pentyl, or α-phenylethyl)[41–43] respectively:

$$L_nM + 3ROOH \underset{-S}{\overset{SH}{\rightleftarrows}} L_nM^{+}(OOR{\cdot}ROOH)^{-} + ROH + H_2O \quad (10)$$

(2) For cobalt pyridine-acetylacetonates[44] and cobalt(II) complexes with Schiff bases, in reactions with t-butyl and cumyl hydroperoxides, to form cobalt(III) peroxides:[44–47]

$$2[Co^{II}] + 3ROOH \xrightarrow[CH_2Cl_2]{20^\circ C} 2ROO\text{–}[Co^{III}] + ROH + H_2O \quad (11)$$

where [Co^{II}] are the complexes

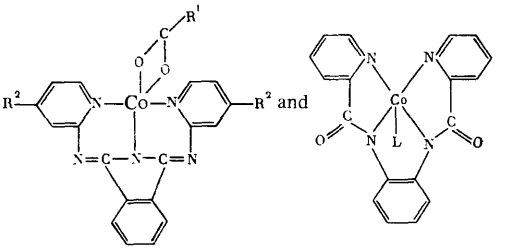


R^1=H; Z=MeN$\langle^{(CH_2)_3}_{(CH_2)_3}$ (Co (NMe salpr)), $(CH_2)_2$ (Co (salen)), OC_6H_4 (Co (salphen)),

HN$\langle^{(CH_2)_3}_{(CH_2)_3}$ (Co (salpr));

R^1=OMe, Z=$(CH_2)_2$ (Co (MeO salen))

and also other Co^{II} complexes: the 1,3-bis-(2-pyridylimino)isoindole and *N,N'*-bis-(2'-pyridinecarboxamido)-1,2-benzene complexes



Co(R^2BPI^{1-}·OCOR^1) Co(BPB)(4-Mepy)

(3) For the iridium complexes IrX(CO)L_2 (L = PPh_3, PPh_2Me, or $AsPh_3$), which react with t-butyl and cumyl hydroperoxides to give either mono- (X = I) or bis-alkylperoxides (X = Cl, Br):[48–50]

$$IrI(CO)L_2 + ROOH \rightarrow Ir(H)I(OOR)(CO)L_2 \quad (12)$$

$$IrX(CO)L_2 + 2ROOH \rightarrow \begin{matrix}L\\OC\end{matrix}\!\!\begin{matrix}OOR\\|\\Ir\\|\\X\end{matrix}\!\!\begin{matrix}OOR\\|\\L\end{matrix} \quad (13)$$

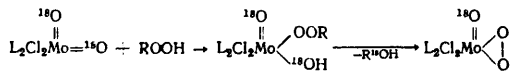
The complex Ir(H)I(OOR)(CO)L_2 is unstable and is converted to the more stable peroxide Ir(CO)(OOR)I_2L_2 by successive elimination of HI and addition of I_2.

Reaction (8) has been studied in detail as one of the effective methods of inhibiting radical-chain processes involving ROOH or O_2.[51–67] The reaction occurs for TMC's in various groups of the Periodic Table.

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† Reaction (7a) includes oxidation of the initial metal complex to the hydroxide $L_nM^{+}OH^{-}$, the reaction of which with ROOH [Eqn.(3)] also gives the desired product.

An example of Eqn.(9) is the formation of alkylperoxide complexes from the labelled oxo-complex of molybdenum $L_2Cl_2Mo(^{18}O)_2$:[9]



(14)

The possible preparation of alkylperoxide complexes by the reaction of TMC's with ROOH is also discussed in a number of papers on the specific synthesis of these compounds—derivatives of titanium,[68] zirconium,[69] vanadium,[21-26] chromium,[40], and molybdenum,[41] in numerous papers on the hydroperoxide catalytic oxidation of substrates of various kinds (alkenes, alkanes, alcohols, ethers, amines, etc.) on vanadium,[70-76] chromium,[77,78] molybdenum and tungsten,[9,10,70-75] manganese,[79] rhodium,[3-10,80-86] iridium, palladium, and platinum,[3-10] and titanium[20,87] compounds, and in studies of the mechanism of the catalysed decomposition of alkyl hydroperoxides.[88,89]

Methods for preparing alkylperoxide complexes are not restricted to reactions of TMC's with ROOH. A considerable number of these compounds are obtained by auto-oxidation of TMC's. If the latter contain a metal–alkyl bond or one emerges during their oxidation, alkylperoxide complexes are usually formed by the insertion of an oxygen molecule into this bond:

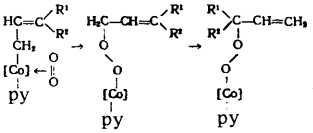
$$L_nM-R+O_2\rightarrow L_nMOOR \qquad (15)$$

Reaction (15) has been studied in greatest detail for the alkylcobaloximes R–[Co]–L.[90-103] Depending on the energy of the Co–R bond, which is determined by the nature of R and the ligand in the axial position, the insertion of oxygen may occur under ambient conditions, on photochemical irradiation, or at high temperatures in a chloroform, acetone, or methanol solution:

$$py-[Co]-R+O_2\xrightarrow{h\nu}py-[Co]-OOR \qquad (16)$$

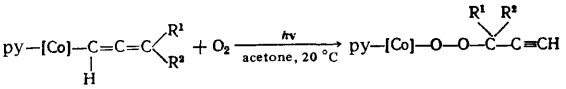
where [Co] represents the cobaloxime.

When R is a substituted allyl group, isomerisation of this group can occur simultaneously with the insertion of oxygen by a concerted mechanism:[97]



(17)

When R is a substituted allenyl or prop-2-ynyl group, in both cases the product contains a prop-2-ynyl radical:



(18)

The mechanism of the insertion of oxygen into the Co–R bond has not been unambiguously established. For the thermal insertion [py(Dmg)$_2$Co–R complexes] three possible mechanisms are proposed: a radical,[96] cryptoradical,[97] and molecular[97] mechanism. Data on the thermal stability of alkylcobaloximes and the kinetics of their oxidation[94,97] agree to a large extent with the cryptoradical mechanism:

$$RCoL\overset{\Delta}{\rightleftharpoons}\{R^{\cdot}\cdots\dot{C}oL\} \qquad (19)$$

$$\{R^{\cdot}\cdots{}^{\cdot}CoL\}+O_2\rightarrow ROOCoL \qquad (20)$$

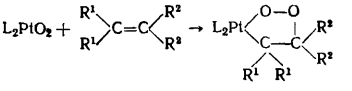
According to data in Ref.102 the mechanism of the photochemical insertion of oxygen into the Co–C bond can be described by reactions (19) and (20), the only difference being that the formation of the radical pair is initiated by light, although the role of light in the mechanism of photochemical oxidation of alkylcobaloximes has not been unambigously established.[97,101,104]

The production of tungsten benzylperoxide R_3WOOR from hexabenzylditungsten (–74 °C) not only touches on the metal–carbon bond but also on the metal–metal bond.[69,105]

The formation of platinum peroxides by Eqns.(21) and (22) [106-108] provides an illustration of a method for producing alkylperoxide complexes by the oxidation of an M–R bond formed *in situ*.

$$LPtMe_2+RI+O_2\rightarrow LPtMe_2(I)OOR \qquad (21)$$

(L = 1,10-phenanthroline or bipyridyl: R = Pr^i or But^t);

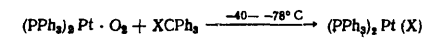


(22)

[R^1 = Me, R^2 = CN; R^1 = R^2 = CN; L = PPh_3, P(cyclo-C_6H_{11})$_3$].

Reaction (21) may also have a radical non-chain mechanism, including a reaction of the platinum complex with RO_2 radicals.[107]

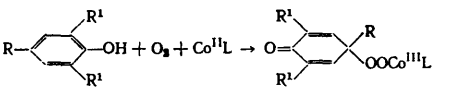
The formation of a C–Pt bond in the reaction of the oxygen complex $(PPh_3)_2Pt.O_2$ with $XCPh_3$ (X = Cl, Br) according to Eqn.(23) is unlikely on steric grounds:[108]



(23)

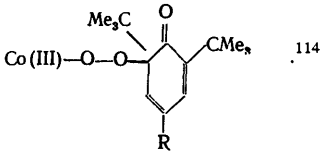
Indirect evidence for the formation of alkylperoxide complexes in accordance with Eqn.(15) has been obtained in studies of the processes of auto-oxidation of other TMC's with σ-bonded organic ligands, viz. $Cp_2Zr(R)Cl$,[34] tetrabenzylzirconium and tetrabenzylhafnium, dialkylzirconocene and dialkylhafnocene,[69,105] the zirconium complex $(tritox)_2ZrMe(OCMe_2CH=CH_2)$ (tritox = Bu^t_3CO),[109] and hexakis(trimethylsilylmethyl)dimolybdenum.[69]

The formation of peroxide compounds of the LCoOOR type on auto-oxidation of cobalt salfuryl [sic?; Schiff base ligands based on salicylaldehyde and amines (Ed.of Translation)] complexes, and also pyridinecobaloxime, which do not contain a direct cobalt–carbon bond and do not form one in the intermediate stages of the reaction, is described by Eqn.(24).[45,110,118]



(24)

where L = $(DmgH)_2$py, salpr, NMe(salpr), and other substituted salfuryl ligands and R^1 = CMe_3. Where R is an aryl group the cobalt-peroxide bond is formed in position 2 of the phenyl ring:



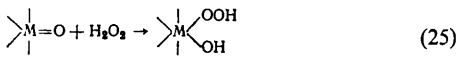
[114]

A distinctive feature of this process [Eqn.(24)] is that the formation of the peroxide CoOOR takes place at the stage where there is a reaction of the phenoxyl radical and the complex $Co^{II}L$, which are formed as intermediates, with the oxygen molecule.[115,118]

2. Transition Metal Hydroperoxides

Transition metal hydroperoxides L_nMOOH are not so numerous as alkylperoxide complexes. Their methods of preparation are in general similar to those described above for L_nMOOR, i.e. based on the reaction of a TMC with either H_2O_2 or molecular oxygen.

The preparation of permolybdic and pertungstic acids by the addition of H_2O_2 to the metal oxides is well known:[119]

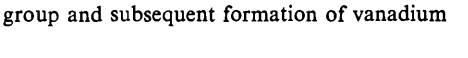


(25)

A similar reaction occurs in the preparation of vanadium hydroperoxides from the complexes $L_nV=O$, where L is picoline.[120] The fact that the vanadyl group is able to react with H_2O_2 but is unaffected by ROOH [see Eqns.(4) and (5) and also Refs.21–26] can be attributed to the higher acidity of hydrogen peroxide compared to an alkylhydroperoxide, which is necessary for the protonation of the vanadyl group and subsequent formation of vanadium hydroxide.

The reaction of H_2O_2 with π-complexes of chromium $(Arene)_2Cr$ and of molybdenum and tungsten Cp_2MX_2 leads to the formation of the hydroperoxides $(Arene)_2Cr^+(OOH.H_2O_2)^-$ [43] and $Cp_2MX_2^+.(OOH.H_2O_2)^-$ [42] respectively. The stoichiometry of the reaction corresponds to Eqn.(10).

The possible reaction of Fe^{II} with H_2O_2 to form the peroxide $Fe^{II}OOH$ has been discussed:[121]

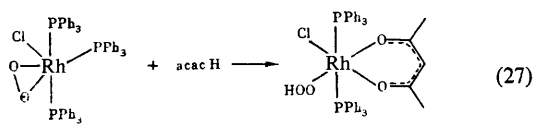


(26)

The substitution of hydroxide, alkoxide, or carboxyl groups attached to the metal by the OOH moiety of hydrogen peroxide in accordance with Eqn.(3) is proposed for the preparation of the vanadium peroxides $V(O)(OR)_2OOH$ and $V(O)(OR)(OOH)_2$ from $VO(acac)_2$,[120] the iron peroxides $[FeL(OH)OOH]^{3-}$ from $[FeL(OH)]^{2-}$ and $[FeL(OH)_2]^{3-}$ (L = ethylenediaminetetra-acetate),[122] and the platinum peroxides $L_2Pt(R)OOH$ from the complexes $L_2Pt(R)OH$, where L = PPh_3, PPh_2Me, $PPhMe_2$, or $P(PhCH_2)_3$ and R = Me, Ph, $PhCH_2$, or CF_3.[32]

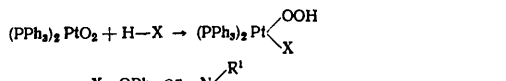
Labile hydroperoxide complexes of platinum $[L_2Pt(OOH)(solv)]^+$ and iridium $Ir(OOH)(Cl_2)(C_8H_{12})$ can be obtained by inserting an oxygen molecule into the M–H bond in the corresponding hydrides $[L_2Pt(H)(solv)]^+$ (L = PPh_3, $PPhMe_2$, or PEt_3; solv = an alkene)[33] or $Ir(H)(Cl)_2(C_8H_{12})$.[123]

Reactions of stable oxygen complexes with compounds that are hydrogen-atom donors are also used to obtain the hydroperoxides L_nMOOH. A rhodium hydroperoxide is produced by the reaction of the dioxygen complex $(PPh_3)_3Rh(Cl)O_2$ with acetylacetone in benzene or dimethoxyethane:[124,125]



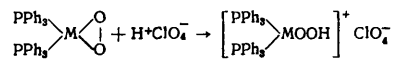
(27)

The reaction of this same dioxygen complex with cyclopentadiene in dimethoxyethane gives the hydroperoxide $(PPh_3)(\eta^5\text{-}C_5H_5)(Cl).RhOOh$. Platinum hydroperoxides are formed by the reaction of $(PPh_3)_2PtO_2$ with imides and phenols:[126]



(28)

Pt, Pd, and Rh hydroperoxides can also be obtained by the reaction of the oxygen complexes $(PPh_3)_2MO_2$ with proton donors:[51,127,131]



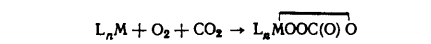
(29)

Consideration has also been given to the possible production of transition metal hydroperoxides as intermediates in the oxidation of the CH bond by a chromium peroxo-complex CrO_5L [L = py, bipy, or phen (1,10-phenanthroline)],[132] the oxidation of water in the presence of manganese complexes,[133] the oxidation with oxygen of a mixture of *p*-nitrophenylhydrazone with the complex Co^{II}(MeO.salen)(py),[116] and also in the oxidation of organic and inorganic substrates by oxygen and H_2O_2 catalysed by Rh, Pd, and Ir complexes.[3–10]

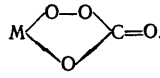
3. Percarboxylate Complexes

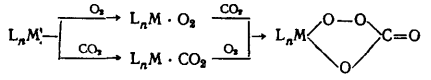
Percarboxylate complexes have been reported for Group VIII metals only.

The oxidation of complexes of these metals with molecular oxygen in a CO_2 medium gives percarboxylate complexes in accordance with overall equation:[128,134–136]



(30)

I.r. and ^1H n.m.r. spectroscopic results[135] and X-ray structure analysis[79] show that the peroxocarbonate ligand is bidentate, forming a five-membered  ring with the metal. Reaction (30) may occur by the insertion of either CO_2 into an  three-membered ring, as is known for compounds of Rh, Ir,[79,135] and Pt,[108,128,134] or an oxygen molecule into a metal–carbon dioxide bond, as is typical of nickel complexes:[137]

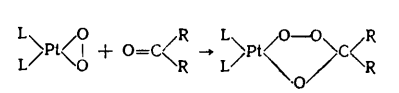


(31)

The reaction of the oxygen complexes $(PPh_3)_2PtO_2$ [138] or $Mn(II)O_2$, where Mn(II) represents a porphyrin complex of manganese,[139] with ClCOPh leads to formation of the perbenzoates $(PPh_3)_2PtCl(OOCOPh)$ or Mn(III)OOCOPh respectively. All the indications are that the process takes place via a stage in which an M–COPh metal–carbon bond is formed.

Perbenzoate complexes of rhodium and iridium can be obtained by the reaction of the complexes $M(CO)(MeCN)(PPh_3)_2ClO_4$ with an excess of the sodium salt of *m*-chloroperbenzoic acid in dichloromethane at 0 °C.[140]

There is a certain similarity between the perbenzoates and the perketyl complexes of platinum which are obtained by the addition of aldehydes and ketones to L_2PtO_2, using a excess of the aldehyde or ketone with respect to the oxygen complex:[106,108,127,128,137]



L=PPh_3, P(C_6H_{11})$_3$; R=CH_3, Ph

(33)

To conclude our report on methods for preparing transition metal peroxide complexes a mention must be made of the similarity in structure between the TMPC's discussed above and the oxygenated

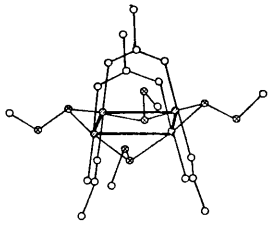
forms of metalloenzymes, e.g. Fe_fOOR, where Fe_f is an iron-containing fragment and R = H, alkyl, or R'CO.

These peroxides are regarded as important intermediates in the oxidation, by molecular oxygen, of myoglobin and haemoglobin in solutions of phenols, amines, and hydrazines[140–142] and of cytochrome P-450 in carboxylic acid solutions,[136,137] the oxidation of horse-radish peroxidase by hydroperoxides ROOH,[146,147] and the catalytic oxidation of substrates of various kinds on metalloenzymes and model systems.[11,148–152]

III. PROPERTIES

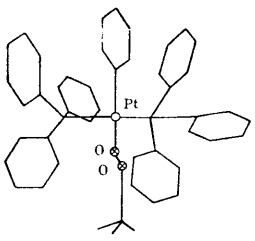
Most of the TMPC's that have been isolated, which number almost 200, are crystalline solids but a few are liquids.

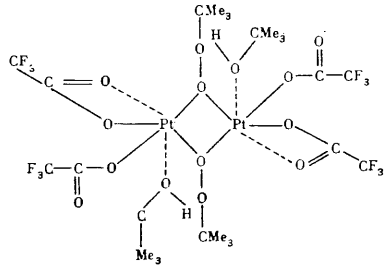
They have a considerably higher solubility in polar solvents than in non-polar solvents owing to a significant amount of ionic character in the bond between the metal and the peroxide moiety. When isolated from solutions TMPC's occur as monomers, dimers, tetramers, and also as associates with hydroperoxides and the corresponding alcohols. The structures of some TMPC's are given below:



$[(CCl_3CO_2)Pd(OOBu^t)]_4$

o – Pd, ⊗ – O in a peroxide group (Ref.28)





trans-$(PPh_3)_2Pt(Ph)(OOBu^t)$ (Ref.32) $(CF_3CO_2)_2Pt(OOBu^t)(Bu^t\text{-}BuOH)]_2$ (Ref.30)

The u.v. spectra of TMPC's, like those of organic peroxides, are not very characteristic and so are comparatively rarely used to study their properties.

Alkylperoxides and hydroperoxides of metals have a medium or strong band due to stretches of the O–O bond in the 815–890 cm^{-1} region. In the percarbonate complexes this band is shifted to lower wavenumbers by 30–60 cm^{-1}. For the hydroperoxide complexes there is also absorption at 3400–3500 cm^{-1} (due to O–H stretches). Bands due to peroxide or OH groups of coordinated ROOH or ROH molecules may be mixed in with these bands.

N.m.r. spectroscopy has been widely used to determine the composition and structure of TMPC's.[22,29,31,32,36,37,48,49,93,124,125] Many of the studies were made using ^1H nuclei. The signal due to the R protons in metal alkylperoxides L_nMOOR may be shifted to either high or low field with respect to the protons in organic peroxides depending on the nature of the metal, the ligands attached to it, and the mutual disposition of the latter in the complex. Valuable information on the structure of TMPC's is obtained from n.m.r. data for ^{13}C, ^{19}F, and ^{31}P nuclei present in the ligands attached to the metal.

The stability of TMPC's varies over a wide range: some TMPC's can exist only at low or moderate temperatures while other withstand heating to 200–220 °C without qualitative or quantitative changes in their composition.

An important physical characteristic of TMPC's is the length of the oxygen–oxygen bond l_{O-O} in them. However these values have a unique character and do not enable any correlations to be made between the l_{O-O} lengths in TMPC's and their structure and thermal stability. One can say only that l_{O-O} can vary over a wide range, 1.22–1.50 Å, in different peroxides.[32,36,37,39,102,106,107,115,117,136]

Notwithstanding the small amount of data on the stability of TMPC's there is quite a definite tendency for it to depend on the nature of the metal, the ligands attached to it, and the nature of R. The stability of peroxides of chromium, molybdenum, and tungsten,[40–42,77,153,154] cobalt,[39,90–94,96–98] iridium and rhodium,[48–50,140] and palladium and platinum[31,127] decreases in line with a decrease in the electronegativity of the metal and the electron-acceptor properties of the ligands attached to it. A tendency for the stability of the TMPC to decrease is also observed on increasing the electron-accepting function of the radical R attached to the peroxide group.[83,148–150,155] The influence of the nature of R is clearly shown by comparing the stability of metal hydroperoxides and alkylperoxides: as a rule the latter are considerably more stable than the former.[39,40,77,154]

It is readily observed that the stability of TMPC's decreases as the degree of charge transfer from the metal to the peroxide moiety increases. This is confirmed, for example, by the displacement of the O–O stretching band in the i.r. spectra to lower wavenumbers[31,48–50,127] and the shifts of the resonance lines of the protons in the radical in the ^1H n.m.r. spectra of TMPC's to lower fields when the electron-donor properties of the ligands attached to the metal are increased.[31] The occurrence of this interrelationship between the stability of a TMPC and the degree of charge transfer to the O–O bond is quite reasonable because an increase in the population of the antibonding orbital of this bond leads to a reduction in its energy and bond order and hence to a decrease in the overall stability of the peroxide complexes. From this viewpoint the formation of the associates $(MOOR)_n$[28–30,156] or MOOR.ROH[29] and MOOR.ROOH[41–43,154] can be regarded as a stabilising factor for the TMPC[116,154] resulting from partial delocalisation of the excess of electron density from the O–O bond to the coordinated molecules. The trends in the variation in stability of TMPC's discussed above are characteristic of both the crystalline state of these compounds and their solutions. However, the stabilities of TMPC's are usually appreciably lower in the presence of solvents, especially strongly basic solvents, than in their absence.[36,45,50,112,140,154,157] The effect of the solvents may be that they facilitate either disruption of the associates $MOOR.X_n$ (X = MOOR, ROH, ROOH), which are more stable than the monomeric form MOOR, or an increase in the degree of charge transfer from the metal to the O–O bond, forming donor-acceptor type complexes with the MOOR:

$$M^{\delta+}OOR^{\delta-} + L \rightleftharpoons L \rightarrow M^{\delta+}OOR^{\delta-} \quad (|\delta_1| > |\delta|)$$

Furthermore, the solvents may react chemically with the TMPC's by various routes which arise from both the polar covalent or ionic character of the M—OOR bond and the labile nature of the O—O bond.

In view of what has been discussed above we shall consider the reactions of TMPC's in solution, which can be provisionally divided into three types: (1) reactions with preservation of the MOOR moiety; (2) protolysis or hydrolysis of the peroxide group; and (3) cleavage of the peroxide group.

Reactions of the first type include protolysis of the ligands attached to the metal[158] or their replacement,[94,158] both of which occur with cobalt alkyl peroxides:

$$\underset{(R = CHMe_2,\ L = H_2O)}{ROOCo(DmgH)_2L} + H^+ \rightleftharpoons [ROOCo(Dmg_2H_2)L]^+ \quad (34)$$

$$LCoOOR + H_2O \rightleftharpoons H_2O \cdot CoOOR, \quad (35)$$

(L = pyridine, piperidine, or 2-methylpyrazine; R = Me, Et, Pr^i, Ph).

Reactions analogous to (34) and (35) can be regarded as intermediate stages in the protolysis and hydrolysis of peroxide groups, which occur for peroxide complexes of various metals:[45,50,94,158]

$$L_nMOOR \xrightarrow[(a)]{H^+X^-} L_nMX + ROOH \quad (36)$$

$$L_nMOOR \xrightarrow[(b)]{H_2O} L_nMOH + ROOH, \quad (37)$$

where H^+X^- is a carboxylic or mineral acid.

Reaction (36) [108,154] usually proceeds at a rapid rate, indicating that the M—OOR bond is appreciably ionic. If HX is a mineral acid the process can be explosive and accompanied by decomposition of the ROOH product.[154] The polar character of the M—OOR bond accounts for the instability of cobalt alkylperoxide complexes in chlorine-containing solvents such as chloroform and dichloromethane[45] and of platinum TMPC's in alkyl bromides;[108] this may be due to a reaction of these TMPC's with the C—halogen bond in the solvent:

$$(salen)CoOOBu^t + R\text{-}Cl \rightarrow (salen)CoCl + ROOBu^t \quad (38)$$

If the M—OOR bond is weakly polar, as in peroxide complexes of Pd,[28] the OOR group can be exchanged with an alkene (all the better if the double bond is internal rather than terminal):

$$CF_3C(O)OPdOOBu^t + \text{alkene} \rightarrow CF_3C(O)OPd\text{-alkyl} + Bu^t\text{-}BuOOH \quad (39)$$

An oxidation-reduction process can occur in a TMPC:

$$L_nM^+OOR^- \rightarrow L_nM^0 + RO_2^{\cdot} \quad (40)$$

This reaction is known as one of the methods for generating $RO_2^{\cdot}$ radicals[139,159] in a transition metal complex—hydroperoxide system.

Reactions of TMPC's which are accompanied by decomposition of the peroxide group are the most numerous. In accordance with the effect of M, L, and R on the stability of the peroxide complexes L_nMOOR, as discussed above, the most probable route for the decomposition of these compounds is rupture of the O—O bond[9,26,104,157] which may occur by either a homolytic or a heterolytic mechanism, and may be unimolecular or bimolecular.

The spontaneous homolysis of the O—O bond leads to formation of a radical pair [Eqn.(41)], the fate of which depends on the nature of the metal-complex radical (i.e. the oxidation state of the metal and its ligand environment), the nature of the solvent, etc.:[17,19,26,49,118,160]

$$L_nMOOR \rightarrow L_nMO^{\cdot} + {}^{\cdot}OR \quad (41)$$

The kinetic and activation parameters of reaction (41) have been determined for $(EtO)_3TiOOCMe_3$.[160] The activation energy of the process is low, 50.2 and 79.5 kJ mol^{-1} in CCl_4 and ethylbenzene respectively. A similar value for the activation energy (54.4 kJ mol^{-1}) was found for the homolysis of the peroxide bond in the cobalt complex $Co^{III}(BPI)(OAc)(OOBu^t)$.[118]

Heterolytic rupture of the O—O bond was proposed in Refs.2 and 9 and confirmed for percarboxylate complexes of iron:[145]

$$L_nM^{+n}OOR^- \rightarrow (L_nMO)^{+n} + RO^- \quad (42)$$

Rupture of the O—O bond can occur by the reaction of the peroxide moiety of a TMPC with a C—H bond in the solvent, especially if the latter has a mobile hydrogen atom:

$$L_nMOOR \xrightarrow[-R^{\cdot}]{R'\text{-}H} L_nMOH + RO^{\cdot} \quad (43)$$

It has been shown, in the case of the cobalt peroxides LCoOOR (L = salpr, R = *p*-quinol), that TMPC's can be reduced by alcohols (other than tertiary) to the corresponding hydroxides (at 10° to 20 °C).[112] The alcohols are converted to the corresponding aldehydes. The rate of the reaction increases with increasing acidity of the hydroxy groups and mobility of the α-hydrogen atoms in the ROH. Two possible mechanisms are proposed for this reaction [Eqns.(44) and (45)], both of which involve rupture of the O—O bond:

$$LCoOOR + R''CHOH \rightarrow \text{cage} \rightarrow ROH + R''CHO$$
$$LCoOH \leftarrow R''CH_2OH \quad LCoO^{\cdot} \quad (44)$$

$$LCoOOR + R'OH \rightleftharpoons \text{cage} \rightarrow LCoOH + ROH + R''CHO \quad (45)$$

The concerted mechanism for the transfer of hydrogen atoms to the peroxide bonds seems more preferable, since it corresponds more to the effect of the nature of the R'OH on the rate of the reaction and to the polar character of the Co—OOR bond, which favours the formation of hydrogen bonds.

Under mild conditions (0 °C, methanol or diglyme as solvent) pyCoOOR (R = benzyl, propyl, or cyclohexyl) are reduced by the $NaBH_4$/NaOH system again with cleavage of the O—O bond:[92,97,99]

$$PyCoOOR \xrightarrow[NaOH]{NaBH_4} ROH + PyCoOH \quad (46)$$

Reductive rupture of the O—O bond in the platinum phenylethylperoxide $(Ph_3P)Pt(Br)OOCH(Me)Ph$ under the action of lithium hydroaluminate also takes place under very mild conditions (-78 °C, THF solvent).[108]

If the decomposition of the TMPC involves more than one molecule there may be not only destruction of the peroxide group but also a redistribution of the non-peroxide ligands between the metal atoms of the TMPC molecules taking part in the reaction; this occurs in reactions of the complex $IrCl(OOBu^t)(OCOCF_3)(CO).(PPh_3)_2$.[50]

Changes in a TMPC, which are accompanied by the loss of the peroxide oxygen, may also occur by intramolecular oxidation of a metal–carbon bond or a ligand attached to the metal of a donor-acceptor type, and also as the result of a bimolecular reaction with substrates of various kinds (S).

Reactions of the first type are known for peroxides of zirconium,[69] cobalt,[104] and palladium and rhodium:[33,35,125,155]

$$Cp_2Zr(R')OOR \rightarrow Cp_2Zr(OR')OR \quad (47)$$

$$(acac)Cl(PPh_3)_2RhOOH \rightarrow (acac)Cl(PPh_3)RhOH + Ph_3P{=}O \quad (48)$$

Reactions of the second type are more numerous and take place according to the following general scheme:

$$L_nMOOR + S \rightarrow L_nMOR + SO \quad (49)$$

These can be regarded as stages in the transfer of oxygen from ROOH to a substrate in the catalytic oxidation cycle of the latter and are therefore of particular interest in a practical, as well as a theoretical, respect. For this reason it is appropriate to consider TMPC reactions that are described by Eqn.(49) in more detail.

IV. PARTICIPATION IN REACTIONS WHERE THERE IS STOICHIOMETRIC OXIDATION OF ORGANIC AND INORGANIC SUBSTRATES

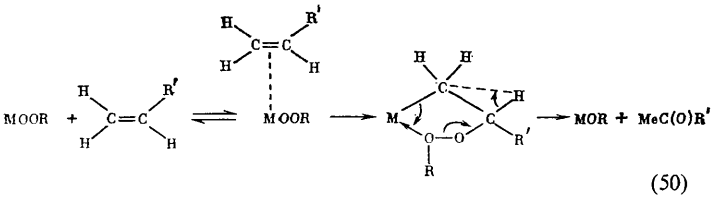
The ability of TMPC's to act as oxygen atom donors in their reactions with organic substrates (alkenes, aromatic hydrocarbons, cycloalkanols, and alkanes) and hetero-organic or inorganic substrates (PPh_3, CO, NO) has been conclusively demonstrated in numerous instances.[28–32,126,156] The ketonisation of alkenes has been investigated in greatest detail. In the temperature range 0° to 100 °C peroxide complexes of Pd and Pt oxidise terminal linear alkanes to ketones with high selectivity.[28–32,157] Iridium (III) alkylperoxides[110] and hydroperoxides[32] are also able to oxidise terminal alkenes. Since many peroxides have the composition $[L_nMOOR]_m$ it is suggested that the active form is the monomeric form produced by decomposition of the associates in solution.[29]

Cyclic and internal linear alkenes are not usually oxidised. Reactions of the latter with t-butylperoxides of Pd are accompanied by displacement of the corresponding hydroperoxide [Eqn.(38)]. At high concentrations of the terminal alkenes the ketone yield decreases owing to competitive exchange of the t-butylperoxy group by the alkene. In the opinion of the authors of Ref.9 the high sensitivity of the ketonisation reaction of alkenes to their structure is due to the predominant influence of steric factors on this reaction. However, the role of electronic factors is no less significant. This is confirmed, for example, by the considerable increase in the reactivity of the peroxide compounds $RCO_2PdOOBu^t$ and $(PPh_3)_2(R')Pt.(OOBu^t)$ towards alkenes when the electron-accepting properties of R [28] and R' [32] respectively are increased:

R	CH_3	CCl_3	C_6H_4	CF_3
Relative rate of ketonisation reaction	1	60	80	130
R'	Ph	<o-NCC_6H_4	<CF_3	—

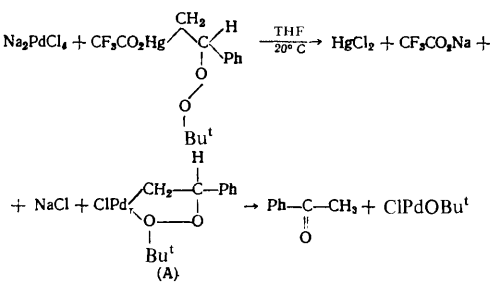
In general, the activity of Pd and Pt peroxides of the composition $L_2(R')MOOR$ as carriers of oxygen to the alkene depends on many factors including the size of the L groups (increasing the volume of L leads to a decrease in the activity of the TMPC) and their mutual orientation (*trans*-forms of alkylperoxides are more active than *cis*-forms), the electronic effects of R' and the nature of R (the hydroperoxides of Pd and Ir are considerably more active than the alkylperoxides of these metals but the reverse is true for Pt peroxides).[32] It is characteristic that, given a similarity in the rules governing the variation of the reactivity of the peroxides as a function of the nature of the ligands attached to the metal, Pd alkylperoxides and hydroperoxides are significantly more active as oxygen carriers than their Pt analogues.[28–32,156]

It is generally accepted[3–10] that the transfer of oxygen from the TMPC to the alkene during its ketonisation takes place by a peroxometallation mechanism, the main stages of which are coordination of the alkene by the metal, formation of a five-membered pseudocyclic intermediate, and its subsequent decomposition to the ketone and an alkoxo- or hydroxo-complex:



(50)

The coordination of the alkene stage is confirmed by the inhibiting effect on the rate of oxygen transfer caused by adding alcohols, strongly complexing solvents (dimethylformamide, hexamethylphosphoryl triamide), and alkenes (1,5-cyclo-octadiene),[28] and also the reduction in the ketone yield in the presence of these substances.[48] The formation of the five-membered pseudocyclic complex was demonstrated by using the reaction of a stable peroxide compound of mercury with palladium salts.[28] The resultant unstable intermediate (A) decomposes to form a ketone:



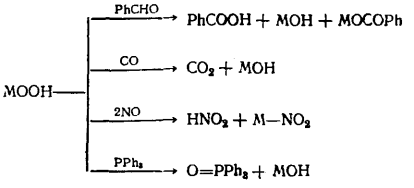
(51)

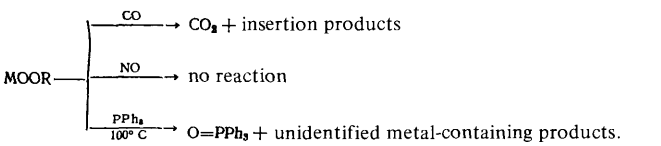
Proof of the formation of a peroxometal ring is also obtained by other preparations of such compounds, which in many cases are fairly stable[108,127,128,134,135,161] [see Eqns.(30), (31), and (33)].

Mechanisms for the decomposition of the ring containing the metal other than that considered in Eqn.(50) are also possible.[9]

Pd and Pt alkylperoxides and hydroperoxides are highly active in oxidising benzaldehyde and a number of inorganic compounds—CO, NO, and PPh_3 (Scheme 1).[31,126]

Scheme 1

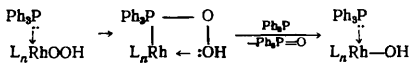




All the reactions except the last take place at 20 °C (THF solvent, nitrogen atmosphere). In these reactions, in contrast to the ketonisation of alkenes, the hydroperoxides of both platinum and palladium are more active than their alkylperoxides; this is indicated by the milder conditions under which the various compounds are oxidised by MOOH and also by the higher reaction rates.

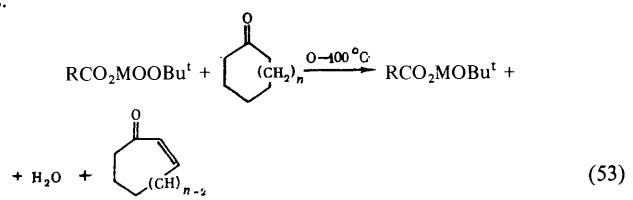
Triphenylphosphine is oxidised in accordance with reaction (49) by treatment with the cobalt alkylperoxide (Bu^tOO)Co(salen) (T = 20 °C),[45] the platinum percarboxylates $(PPh_3)_2PtX(OOCOPh)$, where X = Cl (T = −78 °C) [48] or Br,[103] the rhodium alkylperoxide (1,5-cyclo-octadiene)Rh($OOBu^t$) KBF_4,[33] and the rhodium hydroperoxide $(PPh_3)_2$(acac)(Cl)RhOOH (T = 20 °C).[125,155] The yield of triphenylphosphine oxide is almost quantitative.

The mechanism of the oxidation of triphenylphosphine by the rhodium hydroperoxide[155] (which can be extended to the other reactions in scheme 1 above) involves the formation of a four-membered pseudocyclic complex which undergoes a further reaction with liberation of the products mentioned:



(52)

As oxygen-atom donors the Pd and Pt peroxides $RCOOMOOBu^t$ (R = Me, CCl_3, CF_3) are capable of oxidative dehydrogenation of cycloalkanones (C_5-C_{12}) to the corresponding cycloalkyl-1-en-3-ones.[156]



(53)

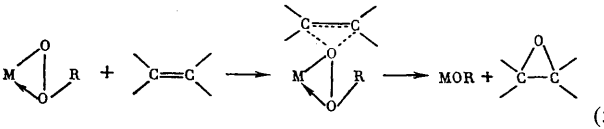
The ability of cobalt alkylperoxides to oxidise alkanes and cycloalkanes, cyclic and acyclic alkenes, and alkylbenzenes to the corresponding ketones, aldehydes, alcohols, epoxides, and peroxides has been noted.[118] In the opinion of the authors the ability of alkylperoxide complexes to oxidise the hydrocarbons listed above depends on their thermal stability. An increase in thermal stability reduces the oxidative properties of the complexes.

Alkylperoxides and hydroperoxides of transition metals (primarily molybdenum, vanadium, and tungsten) are highly selective oxidising agents for converting alkenes to the corresponding oxides. Evidence has been obtained for the participation of MOOR in the alkyl hydroperoxide epoxidation reactions of alkenes—both indirect evidence[70,162] and direct evidence in the case of $(PPh_3)_2ClPt$.$(OOCOPh)$ [48,49] and $Cp_2MX_2^+(OOR.ROOH)^-$ (X = Cl, Br; R = H, t-butyl, cumyl).[163,164] The ability of $Cp_2MX_2^+(OOR.ROOH)^-$ to cause epoxidation depends on the metal (W < Mo), the halide ligand (Cl < Br), R (cumyl < t-butyl), and on the alkene (oct-1-ene < cyclohexene). It is suggested that the active form of the metal alkylperoxide or hydroperoxide is the monomeric form Cp_2MX.$(OOR)^+X^-$, in which the alkylperoxide moiety is attached to the metal by a polar covalent bond:

$$[Cp_2MX_2]^+ OOR^- \rightleftarrows [Cp_2MX(OOR)]^+ X^- \qquad (54)$$

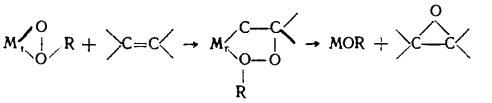
Metal alkylperoxides with a purely or nearly ionic bond between the metal and the peroxide moiety either have no ability to transfer an oxygen atom to alkenes (e.g. the alkali metal salts of organic hydroperoxides[165]) or have a very small ability to do so (e.g. platinum alkylperoxides in strongly electron-donating media[32]). These results indicate that the effectiveness of transition metal alkylperoxides as oxygen carriers depends on the degree of covalency of the M−OOR bond.[164] A similar conclusion was drawn in Ref.10.

The epoxidation of alkenes by the action of Mo, V, and W TMPC's may proceed by the following mechanisms: (1) by a direct reaction of the alkene molecule with the peroxide moiety:[7]



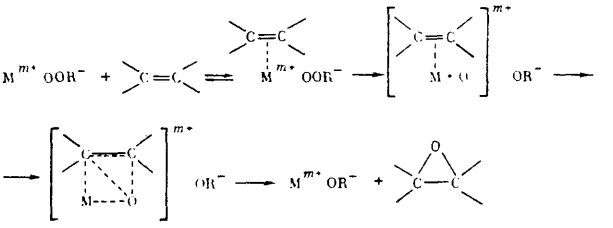
(55)

(2) by a peroxometallation mechanism[3-9,14,15] similar to that discussed above for the ketonisation of alkenes by Pd, Pt, and Ir TMPC's:



(56)

and (3) with the involvement of $(MO)^{m+}$ intermediates (m = 5 for V and 6 for Mo and W),[163] which can be formed from MOOR by heterolytic fission of the peroxide bond[29,145] and can be oxygen-atom donors in the triplet state:

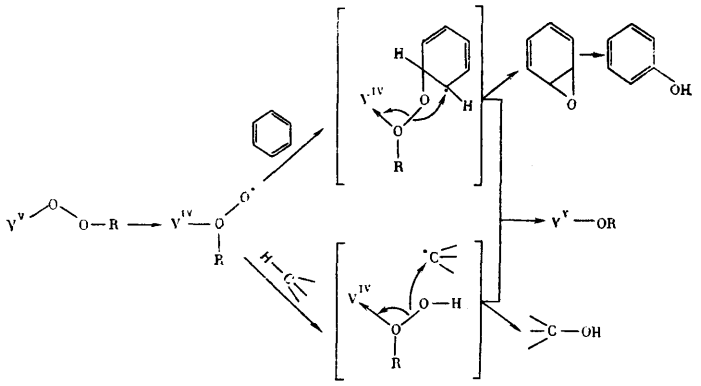


(57)

The vanadium alkylperoxides (dipic)V(O)(OOR)L (R = t-butyl, cumyl; L = H_2O, HMPT) oxidise not only alkenes but also aromatic and saturated hydrocarbons.[36] The selectivity of the processes is usually low. The reactions with alkenes (methylstyrene, butene, cyclohexene, 2-methylpentene) give epoxides (not more than 8% yield) and also the products of oxidative fission and allylic oxidation—aldehydes (10−22%), ketones (4−10%), and alcohols (8−30%).

In contrast to the dipicolinate complexes the compounds (R−OPhsal−R″)V(O)OOR form epoxides with alkenes with a high selectivity,[38] which, in the opinion of those authors, is due to weak coordination of the peroxide oxygen with vanadium; in the dipicolinate complexes the strong coordinate bond between the peroxide oxygen and the hetero-atom hinders coordination of the alkene and consequently inhibits the reaction. A more probable reason for the observed differences in the oxidising properties of the vanadium peroxides is the ability of the dipicolinate alkylperoxide complexes to change into oxygen carriers of a different kind, as is evident from the fact that they oxidise not only alkenes but also aromatic (benzene, toluene, ethylbenzene) and saturated (cyclohexane) hydrocarbons. The latter are oxidised to form hydroxylation products (9−40%), aldehydes (13−27%), and ketones (3−14%).

For the hydroxylation of hydrocarbons by this vanadium alkylperoxide the following mechanism, which is also possible for the oxidation of alkanes, is proposed:



The possible production of octanones by the oxidation of octane with $(Bu^tOO)V(O)(OBu^t)_2$ at room temperature has also been reported.[23,24]

V. PARTICIPATION IN THE CATALYTIC OXIDATION OF ORGANIC AND INORGANIC SUBSTRATES

The formation of TMPC's as intermediates in the catalytic oxidation of organic compounds has been suggested in work on the oxidation of pyrocatechol by oxygen on enzymes containing Fe^{2+}, of the dioxygenase type, and on their model systems,[1,148] and in the oxidation of aromatic compounds and aliphatic alcohols by hydrogen peroxides on an Fe^{III}–pyrocatechol complex.[1,150–152] Similar proposals were subsequently made in a number of papers concerned with the catalytic oxidation of organic[8,10,11,27,31,70–74,110,166–176] and inorganic substrates.[29,31]

Now that a large number of TMPC's have been prepared and their ability to transfer oxygen to organic and inorganic compounds demonstrated (see Section IV), there is no doubt as to the decisive role of these peroxides in the hydroperoxide oxidation of alkenes to the corresponding epoxides on Ti^N, V^V, Cr, and Mo^{VI} complexes[3–10, 69,162,173–178] and to ketones on Pd^{II}, Pt^{II}, Ir^{II}, and Rh^I complexes, [3–10,28,85,116] in the hydroxylation and ketonisation of alkanes on V^V,[23,24] Pd^{II},[1,25] and Co^{III} [46,118] complexes, and also in the oxidation by molecular oxygen of olefins to ketones on Rh^{III} [28] and Pd^{II} [178,179] complexes and phenols to quinones and quinols on Co^{II} complexes.[103,110] The same is true regarding the role of TMPC's in the hydroperoxide oxidation of compounds of phosphorus, sulphur, nitrogen, etc.[31] Generalised schemes have been published for some of the best studied of these catalytic processes.[3–5,10,28,110]

The formation of transition metal alkylperoxides and hydroperoxides as intermediates is energetically very advantageous in catalytic reactions involving molecular oxygen because breaking the O–O single bond in the peroxides requires an energy of 190–250 kJ mol^{-1} [172] whereas dissociation of the oxygen molecule requires 490, 397, or 368 kJ mol^{-1} respectively for the different states $O_2 \rightarrow 2O$ $O_2^* \rightarrow 2O$, and $O_2^- \rightarrow O + O^-$.[1]

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The formation of peroxide compounds with the composition L_nMOOR, where R = H, alkyl, or PhCO, is thus characteristic of the transition metals in almost all Groups of the Periodic Table and can therefore be regarded as one of their inherent fundamental properties; the stability of TMPC's which varies over a wide range, depends on the nature of the metal, the ligands attached to it, the nature of R, and, in solution, on the nature of the solvent, all of which together affect the degree of charge transfer from the metal to the peroxide moiety and hence the energy of the peroxide bond. The most typical routes for reactions of TMPC's are: (a) fission of the peroxide bond, which may be spontaneous (homolytic or heterolytic) or due to an interaction with substrates of various kinds, or (b) intra- or inter-molecular transfer of an oxygen atom to an oxidisable substrate; there are good reasons for supposing that the TMPC's which are intermediates in numerous catalytic processes for the oxidation of organic and inorganic compounds by peroxides are responsible for the transfer of oxygen to the oxidisable substrate.

Further study of methods of preparing TMPC's and their properties will make it possible to determine the nature of the actual carriers of oxygen to substrates of various kinds in the homogeneous, heterogeneous, and enzyme catalysis of the processes for oxidation of these substrates by molecular oxygen and by hydroperoxides and to develop methods for obtaining valuable oxygen-containing products and effective initiating systems for the polymerisation of unsaturated compounds.

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Polymeric Chemical Fibre-reinforced Composite Materials with Reduced Combustibility

L.G.Panova, S.E.Artemenko, N.A.Khalturinskii, and Al.Al.Berlin

The present state of research in the field of the thermal degradation and combustion of fibre-reinforced polymeric composite materials is examined. Special attention has been devoted to questions of the inter-relation between the chemical compositions of the reinforcing fibres and the polymeric binders as well as their thermophysical and thermochemical properties, on the one hand, and the processes occurring on pyrolysis and combustion of the materials, on the other.
The bibliography includes 99 references.

CONTENTS

I. Introduction 680
II. Methods of reducing the combustibility of polymeric composite materials 680
III. Inter-relation between the chemical composition of the reinforcing fibres and polymeric binders and the thermal stability and combustibility of the polymeric composite materials 681
IV. Reduction of the HCN toxicity of the pyrolysis gases from polymeric composite materials reinforced with polyacrylonitrile-containing fibres 683
V. The mechanism of the action of antipyrenes in polymeric composite materials 684

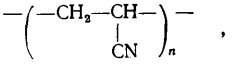
I. INTRODUCTION

Polymeric composition materials (PCM) are at the present time to a large extent responsible for the acceleration of the scientific and technical progress in many branches of the National Economy. The PCM with reduced combustibility, used, for example, in the construction of blocks of flats and public buildings, in transport, etc., are of special interest.

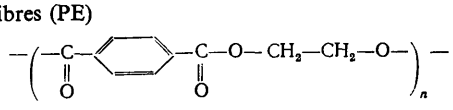
In world practice, polymeric thermoplastic or thermoreactive binders for the synthesis of PCM are reinforced with glass, asbestos, boron, and carbon fibres, aromatic polyamide fibres, and filamental metal oxide, carbide and nitride crystals.[1]

The possibility of reinforcing synthetic resins with chemical fibres manufactured on an industrial scale has attracted the attention of investigators in recent years.[2-22] This is associated with the fact that chemical fibres possess a whole series of specific features which make it possible to extend greatly the range of properties of materials for constructional building purposes: the mass of the articles and components can be greatly reduced, their resistance to vibrations can be increased, they can be stabilised in relation to corrosive media, their antifriction properties can be improved, etc.

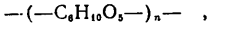
The problem of improving PCM possessing a set of specific physicomechanical properties and reduced combustibility and which are at the same time light, strong, and relatively cheap, can be solved by reinforcing resins with modified chemical fibres produced by the chemical industry on a wide scale, such as polyacrylonitrile fibres (PAN)



polyester fibres (PE)



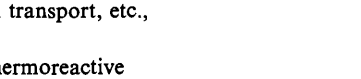
viscose fibres (VF)



poly(vinyl chloride) fibres (PVC)



and copolymeric fibres based on copolymers of acrylontrile and vinyl chloride (AN/VC)



Non-conditioned fibres,[22] which are available both in the chemical fibres industry and in the processing branches of industry (textile, light, etc.),[23] can also be used for this purpose.

II. METHODS OF REDUCING THE COMBUSTIBILITY OF POLYMERIC COMPOSITE MATERIALS

The majority of fibre-filled PCM are combustible materials, which holds back the growth of their manufacture and narrows the region of their applicability and effectiveness. The reduction of the combustibility of PCM is achieved mainly in two ways. The combustibility can be reduced by employing resins containing phosphorus, halogen, nitrogen, etc., compounds which retard or fully suppress combustion and are usually referred to as antipyrenes. Antipyrenes are introduced into the binder at the stage involving the synthesis of oligomers or directly in the formation of the material.[22-34] The second way involves the application of reinforcing systems resistant to combustion: inorganic fibrous fillers (glass, boron, and asbestos fillers); carbon fibre fillers; incombustible thermally stable fibres comprising aromatic polyamides, polyimides, and polyimidoamides; chemical fibres fire-proofed by various antipyrenes.

However, the application of incombustible reinforcing systems without antipyrenes does not solve the problem, because almost the entire polymer matrix burns up in the combustion of the material.[35,36] For example, epoxide PCM containing 60 wt.% of glass fibre

lose up to 40% of their weight when subjected to a test by the "fire tube" method in accordance with GOST 17088-71 [a USSR government standard (Ed.of Translation)].[35]

The reinforcement of combustible polymeric binders with chemical fibres containing an antipyrene makes it possible to improve the resistance to combustion of not only the fibre by itself but also of the polymer matrix.[35–38]

Questions concerning the theory and technology of the preparation of the antipyrene-modified, so called fire-proofed fibres have been described in numerous publications and inventions.[39–83] It is possible to differentiate the following methods whereby resistance to combustion can be imparted to chemical fibres: surface treatment of the fibres with antipyrenes, the introduction of antipyrenes into the polymer before the formation of the fibres, and chemical modification. Various phosphorus-, chlorine-, bromine-, and nitrogen-containing compounds or their synergistic mixtures are used for this purpose.

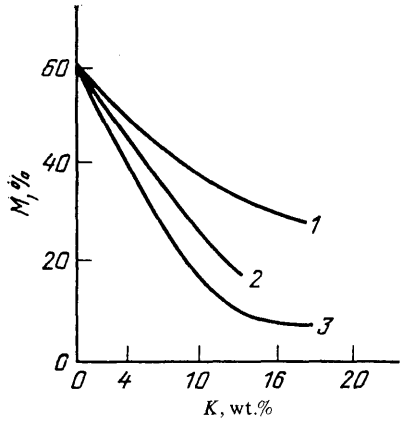


Figure 1. Dependence of the weight loss by the PCM (M) on the amount of inhibitors (K):[37] 1) PAN fibre + SF-342A composition modified with DBPP, Br + P being present in the binder; 2) AN/VC fibre + SF-342A, Cl forming part of the composition of the fibre; 3) PAN fibre modified with DBPP + SF-342A, Br + P being present on the fibre.

The employment of synthetic resins for reducing the combustibility of PCM reinforced with combustible chemical fibres (PAN, VF, PE) is relatively ineffective, since it requires the introduction into the material of large amounts of an antipyrene, which increases its cost and at the same time impairs its physicomechanical properties. In such compositions, it is desirable to introduce the antipyrene not into the polymeric binders but together with the reinforcing fibre.[35–38,84–91] For example, PCM based on anilino-phenol-formaldehyde resin SF-342A and PAN fibres fire-proofed by impregnation with dibromopropyl phosphate (DBPP) is characterised, compared with other materials containing the same amount of DBPP in the binder, by a weight loss smaller by a factor of two (Fig.1, curves *1* and *2*), a lower rate of propagation of the flame, an ignition point higher by 20 K, and an increase in the oxygen index (OI), characterised by the minimum oxygen content in the oxygen–nitrogen mixture ensuring the candle-like combustion of materials and expressed in volume percentages (or volume fractions), from 28 to 34%.

Analogous results have been obtained for phenolic compositions containing antipyrenes with different efficiencies. The Br + P mixture of combustion inhibitors, which is more effective than Cl, reduces the weight loss to a greater extent following the ignition of materials in air when these antipyrenes are introduced into the composition together with the reinforcing fibre [Br + P was introduced with the PAN fibre modified by DBPP, while Cl was introduced together with the reinforcing system comprising a mechanical mixture of PAN and the AN/VC copolymer fibres (Fig.1, curves *2* and *3*)].

However, the Cl entering into the composition of the reinforcing fibre reduces the combustibility of PCM to a greater extent than Br + P introduced into the phenolic resin as part of the composition of DBPP (Fig.1, curves *1* and *2*).

The greater inhibition of the combustion of PCM after the introduction of the antipyrene with the fibre can be explained by the fact that the antipyrene permeates from the fibre to the layer of polymer matrix, protecting thereby both the fibre itself and the polymeric binder against combustion. This has been confirmed experimentally on model PCM specimens prepared by casting in ED-20 epoxide resin lavsan fire-proofed with tricresyl phosphate (TCP).[37] The study of the specimens by scanning electron microscopy combined with X-ray spectroscopic analysis revealed the presence of phosphorus in the boundary layer of the polymer matrix adjoining the fibre over distances exceeding the maximum thickness (5 μm) of the layer of binder in PCM produced by the direct pressing method. The number of pulses recorded over a period of 30 s and characterising the phosphorus content in the specimen was 34 in the reinforcing fibre itself and on moving away from the surface of the fibre into the layer of polymer matrix to distances of 1, 7, 10, 17, and 40 μm the numbers of pulses were respectively 32, 28, 23, 16, and 0.

The antipyrene introduced with the binder permeates into the structure of the reinforcing fibre less effectively and inhibits mainly the combustion of the polymer matrix.[86] This is indicated by the increased weight loss in the combustion of PCM observed when the content of the PAN fibre is increased from 30 to 60% with an unchanged content of the antipyrene introduced into the composition together with the binder (Table 1).

III. INTER-RELATION BETWEEN THE CHEMICAL COMPOSITION OF THE REINFORCING FIBRES AND POLYMERIC BINDERS, AND THE THERMAL STABILITY AND COMBUSTIBILITY OF THE POLYMERIC COMPOSITE MATERIALS

The dependence of the thermal stability and combustibility of unfilled polymers on their chemical structure has been noted in a number of studies.[92–94] It has been shown that (a) there is a correlation between the yields of the coke residue (CR) formed on pyrolysis and the OI of the polymers not containing inhibitors of flame reactions:[92]

$$\mathrm{OI} \times 100 = 17.5 \pm 0.4\,\mathrm{CR};$$

(b) the tendency towards the formation of coke is an additive characteristic of the polymer and can be estimated from the

contributions of the functional groups constituting the polymer units:[92]

$$CR = \frac{\sum(TFC)_i \times 12}{M} \times 100\%,$$

where TFC is the tendency of the group i to form coke expressed in carbon equivalents per polymer unit and M is the molecular weight of the unit; (c) there is a relation between the OI and the heat of combustion per gramme of the test substance:[92]

$$OI = 1.9/\Delta h_{comb},$$

but the relation does not hold for a series of materials, including cellulose, polyacrylonitrile, etc.;[92] (d) there is a relation between the OI and the elemental composition of the polymer.

Table 1. Weight losses in the combustion of PCM containing bromine and phosphorus introduced with the binder.[86]

Br + P content in binder wt.%	Weight loss (%) in different compositions		
	60% PAN fibre + 40% SF-342A resin	50% PAN fibre + 50% SF-342A resin	30% PAN fibre + 70% SF-342A resin
0	60	59	52
2	58	57	46
5	58	50	36
10	49	38	27
15	45	31	—

The thermophysical and thermochemical properties of the fibres have a decisive influence on the characteristics of the thermal degradation and combustion of composite materials reinforced with chemical fibres, such materials constituting multicomponent systems. For example, the temperature of the degradation of the PCM reinforced with PVC and PAN fibres, a mechanical mixture of PAN (60 wt.%) and PVC (40 wt.%) fibres, and AN/VC copolymer fibre is higher by 20–50 K than the temperature of the degradation of the unfilled epoxide resin. The degradation temperatures are directly related to the thermal stabilities of the reinforcing fibres, which can be arranged in the following sequence in terms of this parameter: PAN > PAN + PVC mixture > AN/VC copolymer > PVC.[38]

One of the main characteristics of combustion is the rate of the latter. It can be expressed as the mass velocity characterising the burning up of the material. The rates of pyrolysis of materials under different conditions, including the temperature regimes which obtain on combustion, have been determined from the mass velocity of the degradation reduced with respect to the current mass of the specimen for which the given mass velocity has been found, i.e. with respect to the quantity $\dot{m}/m$, where $\dot{m} = dm/d\tau$, m is the current mass of the specimen in grammes, and τ is the duration of the test in seconds.[38]

The introduction of fibres into epoxide compositions lowers by a factor of 1.5–2 the rate of their pyrolysis and increases by a factor of 2–3 the yields of coke. On the other hand, the presence of fibres in phenolic PCM increases the rate of pyrolysis by a factor of 1.5–3 and lowers the yield of coke by 30–50%. However, the rate of pyrolysis of the material is determined to a large extent by the chemical composition of the fibres, which follows from the fact that the rate of pyrolysis of the unfilled epoxide resin is higher by a factor of 4 than that of the phenolic resin, while the rates of pyrolysis of PCM based on these binders differ by only 20–50%. The same character of the variation of the rate of pyrolysis and of the yield of coke can then be noted for both epoxide and phenolic PCM reinforced with identical chemical fibres (Table 2).[38,87]

Table 2. The mass velocities of the pyrolysis of PCM and the yield of coke at different temperatures:[38]

Reinforcing fibre	Temperature, K				
	673	773	873	973	1073
	Epoxide PCM				
PAN	0.64; 60.0	0.98; 31.0	1.54; 30.0	1.96; 26.5	2.44; 25.0
PVC	0.5; 56.0	0.94; 21.5	1.26; 16.0	1.8; 15.0	2.22; 14.0
AN/VC copolymer	0.65; 47.0	1.15; 27.0	1.75; 23.5	2.4; 21.5	3.0; 20.0
PAN + PVC mixture	0.4; 56.0	0.9; 35.0	1.4; 30.0	1.9; 28.0	2.35; 25.0
ED-20 without fibre	0.4; 53.0	2.5; 25.0	2.8; 9.0	3.35; 9.0	3.9; 9.0
	Phenolic PCM				
PAN	0.45; 79.0	0.78; 64.5	1.1; 61.5	1.4; 58.0	1.6; 55.0
PVC	0.35; 68.5	0.65; 64.5	0.98; 60.0	1.3; 55.0	1.5; 50.0
AN/VC copolymer	0.35; 73.0	0.8; 51.5	1.3; 49.5	1.8; 48.0	2.3; 46.0
PAN + PVC mixture	0.4; 71.0	0.7; 58.0	1.0; 54.0	1.3; 52.0	1.6; 50.0
SF-342A without fibre	0.08; 85.0	0.2; 80.0	0.4; 76.0	0.8; 60.0	1.0; 87.0

*The first figure represents the mass velocity of pyrolysis (s^{-1}) and the second the yield of coke (wt.%).

The chemical composition of the fibres in PCM influences also the temperature in the flame zone, which depends to a large extent on the composition of the pyrolysis gases from the reinforcing fibres.[38] For example, the flame temperature in the combustion of PCM based on PAN fibres is higher by 30 K than in the combustion of the unfilled epoxide resin. The observed dependence of the flame temperature on the amount of chlorine in the reinforcing fibres is complex (Fig.2): in the combustion of materials reinforced with the AN/VC copolymer fibre containing 13% of chlorine, it is higher than in the combustion of PCM based on the mechanical mixture of PAN + PVC fibres (60 and 40 wt.% respectively), containing 9% of chlorine. This is associated with the higher content of the combustible HCN in the pyrolysis gases of the AN/VC fibre compared with the gases evolved on pyrolysis of the mechanical mixture of PAN + PVC fibres (Fig.3).[89] These data show that the combustibility of the material depends not only on the composition but also on the structure of the reinforcing systems.

The ignition delay time is determined by the heat changes accompanying the degradation of the reinforcing fibres.[88] The unfilled epoxide resin has an ignition delay time of 1.3 s. The introduction of PAN fibres into the composition lowers the ignition delay time to 1.0 s, since the degradation of the fibre itself is characterised by an appreciable heat change (Fig.4, curve *3*). The ignition delay times of the PCM reinforced with chlorine-containing fibres, a mixture of

PAN and PVC fibres, which are degraded with smaller heat changes than the PAN fibre (Fig.4, curves *1* and *2*), are longer and amount to 1.8 and 2.2 s respectively. The maximum ignition delay time (2.6 s) is characteristic of PCM with the AN/VC copolymer fibres, whose degradation in the initial stage takes place endothermically (Fig.4, curve *4*).[88]

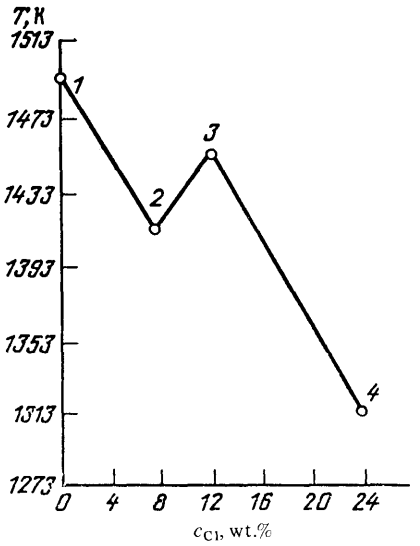
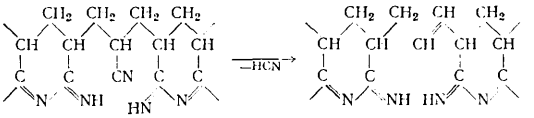
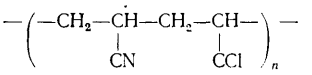


Figure 2. Dependence of the flame temperature (T_f) of epoxide PCM on the chlorine concentration c_{Cl} in the reinforcing fibres:[38] 1) non-reinforced ED-20 epoxide resin; 2) PAN + PVC; 3) AN/VC; 4) PVC.

chain with formation of double bonds via the reaction[99]



The introduction of chlorovinyl groups into the polyacrylonitrile molecule,



prevents its cyclisation, since steric hindrance due to the appearance of unconjugated nitrile groups arises. This increases the amount of uncyclised sections and hence the yield of HCN.[89]

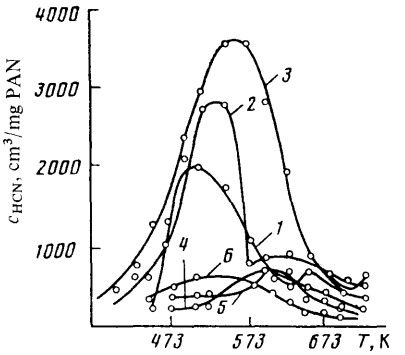


Figure 3. Dependence of the yield of HCN c_{HCN} on the pyrolysis temperatures of various fibres and composite materials based on them:[89] 1) PAN fibre; 2) AN/VC fibre; 3) PCM based on the AN/VC fibres; 4) mechanical mixture of PAN + PVC fibres; 5) PCM based on the PAN + PVC mixture of fibres; 6) PAN fibre modified with 2,3-dibromopropyl phosphate.

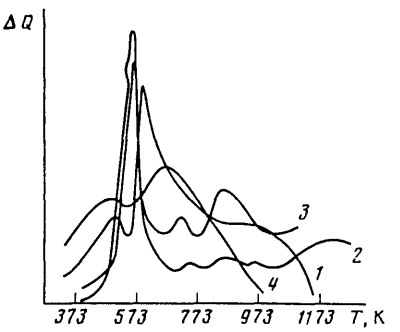


Figure 4. Differential thermal analysis curves for different fibres (Q are the heat changes):[89] 1) PVC fibre; 2) PAN + PVC mechanical mixture; 3) PAN; 4) AN/VC copolymer fibre.

IV. REDUCTION OF THE HCN TOXICITY OF THE PYROLYSIS GASES FROM POLYMERIC COMPOSITE MATERIALS REINFORCED WITH POLYACRYLONITRILE-CONTAINING FIBRES

The polyacrylonitrile-containing fibres used to reinforce resins evolve toxic gases, including HCN, on pyrolysis.[95-97]

A decrease in the HCN toxicity of PCN can be attained in several ways. Thus the amount of HCN evolved from the PAN fibres can be reduced by using graft copolymers of PAN with cellulose. In the pyrolysis of such fibres, the yield of HCN is appreciably reduced owing to a change in the mechanism of the thermal decomposition of PAN: the water evolved on pyrolysis of cellulose hydrolyses the nitrile groups, as a result of which NH_3 is evolved instead of HCN.[98] The AN/VC copolymer fibres used for reinforcement afford an even higher yield of HCN than the PAN homopolymer fibres (Fig.3, curves *1* and *2*).[89] This phenomenon has been explained by the fact that heating of PAN fibres entails complex chemical reactions and structural transformations: cyclisation, aromatisation, and depolymerisation,[97] while the evolution of HCN in the temperature range 473–823 K takes place mainly from the uncyclised sections of the

The second method of reducing the yield of HCN involves the use of a mechanical mixture of the PAN + PVC fibres.[92] Thus the yield of HCN from a mixture of 60 wt.% PAN and 40 wt.% PVC fibres is lower by a factor of ~6 compared with the AN/VC copolymer fibres with the same content of polyacrylonitrile (Fig.3, curves *2*

and *4*). In this reinforcing system, PVC accelerates catalytically the cyclisation of PAN, which reduces the evolution of HCN.[89] The yield of HCN from phenolic PCM reinforced with a mixture of PAN + PVC fibres is close to that observed in the pyrolysis of the reinforcing mixture of fibres (Fig.3, curves *4* and *5*). On the other hand, the yield of HCN from PCM reinforced with the AN/VC copolymer fibres is higher than for the reinforcing fibres (Fig.3, curves *2* and *3*). This has been explained by the different chemical mechanisms of the degradation of the above reinforcing systems, leading to a difference between the degradation reactions of the PCM based on them.

According to differential thermographic (DTA) data (Fig.4), an exothermic peak characteristic of the PAN cyclisation process is observed in the thermal degradation of both PAN fibres and the mixture of PAN + PVC fibres in the same temperature range.[89] For an AN/VC copolymer fibres, an endothermic peak characteristic of the dehydrochlorination processes is observed in the same temperature range, while the exothermic peak corresponding to cyclisation is displaced towards higher temperatures. Since the degradation of the phenolic resin occurs at higher temperatures compared with the AN/VC fibres, the HCl evolved in the dehydrochlorination process accumulates in the bulk of the material, leads to the depolymerisation of PAN, and increases the yield of HCN compared with that observed from the AN/VC fibres alone.[89]

An effective method of reducing the amount of HCN involved consists also in modifying the PAN fibres with dibromopropyl phosphate $(CH_2-Br-CHBr-CH_2O)_3PO$ (Fig.3, curve *6*).

Table 3. The yield of water and HCN in the pyrolysis of fibres.[86–88]

Fibre	c_{H_2O}, cm^3/mg PAN at different temperatures, K				c_{HCN}, cm^3/mg PAN at different temperatures, K			
	423	523	623	723	523	623	723	823
PAN	155	210	150	80	1050	2600	480	180
PAN + 11 wt.% (Br + P)	75	520	710	320	310	750	220	55

V. THE MECHANISM OF THE ACTION OF ANTIPYRENES IN POLYMERIC COMPOSITE MATERIALS

It has been established[93] that various compounds containing isotypical combustion inhibitors have different types of influence on the combustibility of polymers. Bromine-, chlorine-, and phosphorus-containing antipyrenes or their synergistic mixtures exert an inhibiting effect on a series of specific PCM.[37,38,84–89]

The bromine + phosphorus system introduced into the composition of the PAN fibres fire-proofed with dibromopropyl phosphate acts on phenolic PCM [86–88] and alters the course of the reactions in both condensed and gas phases. The composition of the pyrolysis gases changes under these conditions—the water content c_{H_2O} increases and the HCN content c_{HCN} diminishes (Table 3), the amount of heat evolved is reduced, which slows down the reaction in the gas phase, the flame temperature T_{fl} diminishes, the ignition temperature T_i increases, and the yield of coke falls slightly (Table 4).

Table 4. Characteristics of the thermal degradation and combustion of PCM (1 : 1 fibre : resin ratio).[86–88]

Composition	Coke residue (%) at different temperatures, K					T_i, K	T_{fl}, K	OI, %
	673	773	873	973	1073			
PAN + SF-342A	79.0	64.5	61.5	58.0	55.0	1383	1537	27
[PAN + 11 wt.% (Br + P)] + SF-342A	71.0	60.5	56.5	55.0	54.0	1437	1483	34

The introduction of antimony trioxide (Sb_2O_3) into PVC fibre + epoxide resin + polyethylenepolyamine compositions slows down the smoke formation process, increases the yield of coke, lowers the weight loss on combustion, and increases the OI and the ignition temperature (Table 5).[90,91]

Table 5. The influence of Sb_2O_3 on the characteristics of the combustion of epoxide PCM reinforced with PVC fibre.[93,94]

Combustion inhibitor and its content, wt.%	OI, %	Weight loss, %	T_i, K	Yield of coke (%) at different temperatures, K		
				773	873	973
Cl (23.9)	29.0	67.0	1392	21.5	16.0	15.0
Cl (23.9) + Sb_2O_3 (10)	38.0	10.5	1440	29.0	25.0	23.0

In compositions with a phenolic resin reinforced with the AN/VC copolymer fibres, the action of Sb_2O_3 is manifested by an increase (almost by a factor of 2) in the amount of coke residue, a decrease in smoke formation, and a decrease in the weight loss on combustion.[86,88]

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Chemical Principles of the Biotechnology of the Preparation of Fuel

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The chemical aspects of the biotechnology of the preparation of fuels together with the potential resources and possibilities of the biofuel technology are described. The present state of research into the preparation of biogas (mixture of methane and carbon dioxide), ethanol, acetone, butyl alcohol, and hydrogen from the biomass is examined. The technological features and economic aspects of the processes listed above are analysed.
The bibliography includes 213 references.

CONTENTS

I. Potential resources and possibilities of the biofuel technology 687
II. Biogas 688
III. Ethanol 693
IV. The acetone-butyl fermentation 697
V. Hydrogen 699
VI. Conclusion 700

The last decade has been characterised by an increasing interest in the problem of the application of renewable sources of energy. One of the main aspects of this research is associated with the use of solar energy. In recent years, biotechnological methods for the conversion of solar energy into fuel have developed significantly. The world interest in this problem is high, numerous symposia, conferences, and seminars being held annually.

A new scientific and technical field concerned with "fuel from the biomass" has been developed fairly vigorously in our country.[1-6] A number of projects have reached the level of technical solutions, whereas other are passing through the stage of laboratory research and experimental tests.

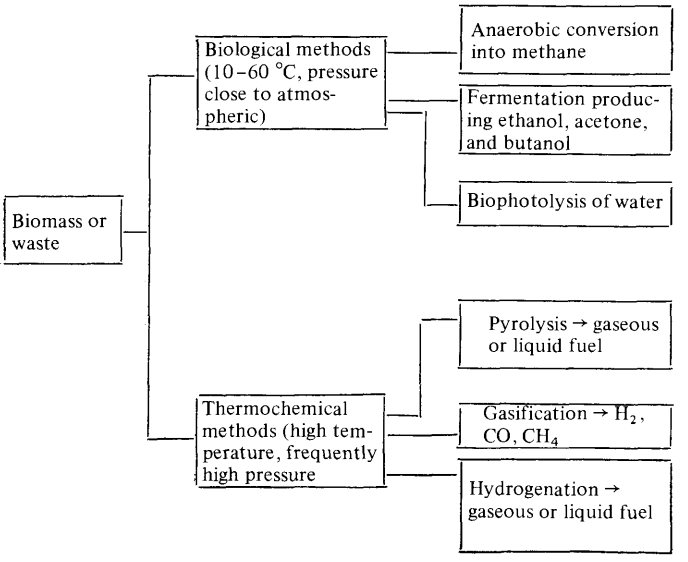
I. POTENTIAL RESOURCES AND POSSIBILITIES OF THE BIOFUEL TECHNOLOGY

The biomass is the cheapest form of renewable energy which can be accumulated on a large scale. By the term biomass, we understand any materials of biological origin, metabolic products, and the organic waste formed in the course of their processing. The daily increment in the biomass on Earth is 200 billion tonnes, which have an energy equivalent of 3×10^{21} J.[7,8]

The systems for the conversion of energy by preparing biofuels are fairly varied and include processes involving the preparation of methane, hydrogen, ethanol, methanol, butyl alcohol, and acetone as well as a number of other components of interest as fuel materials. The overall possibilities of the biofuel technology are fairly considerable and have been discussed in a review.[9]

The products derived from natural vegetation, agricultural waste, a wide variety of industrial waste and waste produced by the municpal economy and finally the crops specially grown in the so called "energy plantations" (sugar cane, manioc, potatoes, plankton, etc.) are potential raw materials for the production of biofuel.

The energy content of certain types of fuel, waste, and biomass are presented in Table 1. The simplest method of extracting energy from many materials is their combustion. Other methods of processing the initial raw material are presented in the Scheme below:



Estimates of the potential contribution of biofuel to the overall energy provision to the community are of fundamental importance. Evidently, biofuel technology may serve as a basis of new power engineering in the developing countries which have relatively poor energy resources but are located in zones with a high bioproductivity. Estimates of the percentage contribution of biofuels in highly developed countries are the subject of lively discussion in the literature.

The utilisation of the biomass in the USA amounts nowadays to 2% of the total energy consumption (1.5 quad g^{-1} or 1.6×10^9 GI g^{-1}).† Various estimates for the year 2000 range from 4 quad g^{-1} (4.2×10^9 GI g^{-1}) to 17 quad g^{-1} (1.8×10^{10} GI g^{-1}). The latter quantity amounts to 15-20% of the total energy production in the USA.[11]

† 1 quad corresponds to 10^{15} British Thermal Units, each of which is equal to 1.06×10^9 GI. This quantity corresponds to approximately 50 million tonnes of coal [Ed.of Translation].

Considerable attention has been devoted to prospects for the utilisation of renewable energy sources in europe. The problem of the preparation of biogas which has been subjected to a detailed and thorough analysis for various European countries.[10-12] The principal conclusion reached in these investigations is that biofuels will play a significant role in the power generation in these countries. By the year 2000, the contribution of the biotechnology of the preparation of fuel to the overall energy requirements of the countries in the Common Market will be 5–10%. For comparison, we may point out that the production of hydroelectric energy in the overall energy balance is only 2%.

Table 1. The energy contents of certain types of fuels, waste, and biomass.[10]

Fuel	Energy content, MJ kg^{-1}	Biomass and waste	Energy content, MJ kg^{-1}
Coal	29 3	Typical biomass	14.0
Coke	28.4	Bacteria	22.7
Dry ash-free peat	21.0	Algae	20.0
Air-dry peat (25% H_2O)	16.3	Straw (15% H_2O)	14.2—15.5
		Dry straw	17.0
Brown coal	14.7	Grassy materials	17.5
Lignite, commercial fuel	26.8	Natural plants	18.3
		Wet wood	16.0
Unrefined petroleum	42.3	Dry ash-free wood	18.7
Diesel fuel	41.0		
Petrol	43.5	Unpurified waste	9.0—11.0
Kerosine	45.6—47.8	Fuel waste	14.7—15.6
Purified gas	41.0	Cattle manure	21.4
Natural gas[a]	31.7—39.8		
Coking gas[a]	16.1	Pig manure	20.0
Hydrogen[a]	12.1	Monosaccharides	15.5
Methane[a]	37.7	Polysaccharides	17.6
Biogas (60% CH_4)[a]	22.3	Lignin	31.1
Methanol	22.4	Protein	23.9
Ethanol (95%)	28.2	Fat	31.4
Ethanol (100%)	29.7	Carbohydrates	16.7—17.6
Isopropyl alcohol	33.0	Unpurified fibre	18.8—19.7
n-Propyl alcohol	33.6		
n-Butyl alcohol	36,2		

[a]Energy content in MJ m^{-3}.

The role of the biomass in the energy supply in the countries of Latin America has been analysed and it has been shown that 10–20% of the overall energy requirement in these countries will be met by employing the biomass and the biotechnology for its conversion into fuel.[13]

The energy programme in China has been discussed[14,15] and it has been shown that up to 30% of the energy provision in that country will be achieved by employing biofuels.

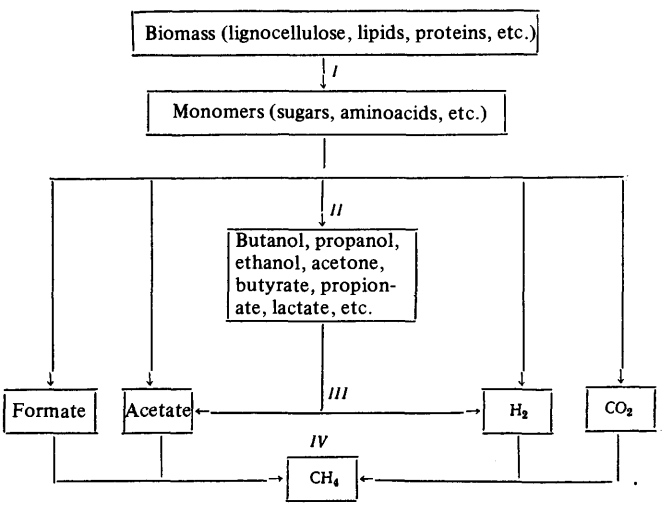
The ecological problems of the utilisation of the biomass and the advantages associated with it have been discussed.[16]

II. BIOGAS

The technology of the preparation of biogas (a mixture of 50–80% of methane and 20–50% of carbon dioxide) by the anaerboic conversion of various types of plant raw materials and organic waste has been developed to the greatest extent.[17-20] At the present time, studies in this field are being prosecuted both within the framework of fundamental research into the formation of methane by complex microbial populations and within the framework of the creation of an improved technology for the intensification of the process.

1. Principles of the Preparation of Methane

The anaerobic conversion of the biomass into methane (methane fermenation) is a complex multistage decomposition of a wide variety of organic materials under anaerobic conditions under the influence of bacterial flora, whose final result is the formation of methane and carbon dioxide. According to modern ideas, the anaerobic conversion of virtually any biomass into methane proceeds via four successive stages: the stage involving the hydrolysis (cleavage) of complex biopolymer molecules (proteins, cellulose, lipids, etc.) into simpler molecules, for example, monomers: aminoacids carbohydrates, etc.; the stage involving the fermentation of the resulting monomer to still simpler substances—lower acids and alcohols; the acetogenic stage (the formation of H_2, CO_2, formate and acetate), and then directly the methanogenic phase, which leads to the final cleavage product—methane:[19,21]



The study of the kinetics of methanogenesis from various substrates (cellulose, hemicelluloses, monosaccharides, ethanol, methanol, butyrate, and acetate) has been described in a number of communications,[21-29] kinetic schemes have been devised, and computer models describing processes involving the formation of methane in such systems, in the presence of natural methanogenic microbial populations, the *Methanobacillus kuzneceovii* system, and the pure *Methanosarcina vacuolata* have been constructed. As an example, Fig.1 illustrates the dynamics of the anaerobic conversion of glucose into methane in the presence of the methanogenic *Methanobacillus kuzneceovii* system. The overall experimental data accumulated as a result of the study of this process are summarised by the following kinetic scheme:

$$C_6H_{12}O_6 + H_2O \rightarrow 2H_2 + 2CO_2 + C_2H_5OH + CH_3COOH,$$
$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2,$$
$$CH_3COOH \rightarrow CH_4 + CO_2,$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O.$$

The first two reactions are formed by a non-methanogenic microorganism via the Embden–Meyerhof pathway and the third and fourth reactions are performed by acetate- and water-utilising methanologens.

A mathematical model of the process, consisting of a system of nine non-linear differential equations, has been devised on the basis of the proposed kinetic scheme.[27-29] The adequacy of the proposed model has been tested by solving the so called direct problem. On the other hand, the solution of the reverse problem made it possible to determine from the available experimental data the kinetic parameters and constants for the conversion of glucose into methane. Mathematical calculations have confirmed the satisfactory quality of the description of the experiment.

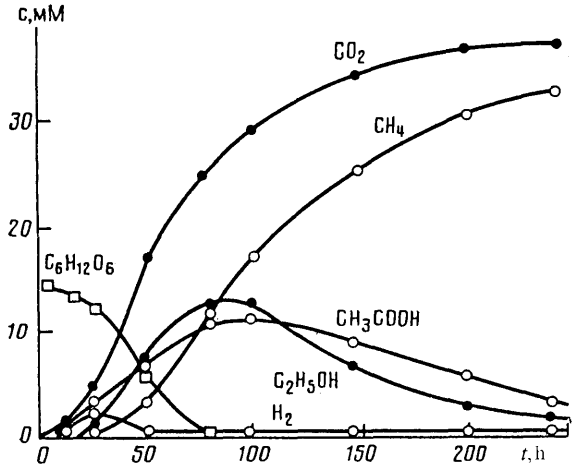


Figure 1. Dynamics of the anaerboic conversion of glucose in the presence of the *Methanobacillus kuzneceovii* system of microorganisms.[24]

Methane fermentation can occur in the temperature range from 10° to 65 °C. It has been shown that thermophilic methane fermentation (45–65 °C) is 2–3 times faster than mesophilic fermentation (25–30 °C), the change in temperature influencing only the rate of the process but not the qualitative composition of the product formed.

The acid generating stage, determined by the activity of the primary anaerobes, occurs at pH from 5 to 6.5–7 and is characterised by an intense growth of bacteria which ferment free carbohydrates. This period is accompanied by a decrease in the content of carbohydrates in the medium, a decrease in the pH of the medium, and an increase in the overall content of volatile aliphatic acids represented by formic, acetic, propionic, butyric, and other acids. Propionic and butyric acids predominate during this period.[17,21,30] The microbiological and biochemical processes in this stage have so far been studied inadequately.[17,20,34]

Among the large group of acid generating bacteria, acetogenic, lactic acid, and butyric acid bacteria as well as producers of caproic and succinic acids, ethanol, butanol, and other lower alcohols and ketones are of special importance (in the literature, this entire group is frequently referred to as solvent synthesising bacteria).

A definite interest has arisen in recent years in a comprehensive investigation of anaerobic bacteria active in the acid generating stage, which are important not only from the standpoint of methane generation but also because they are direct producers of biofuel substances.

2. Methane Forming Bacteria

Methanogens are obligatory anaerobes sensitive to oxygen. The oxidation–reduction potential of the medium used for their growth is -300 mV and less.[31] More than 45 species of methane forming bacteria are known at the present time.

Depending on the species, methanobacteria, can use a limited number of substrates as sources of energy (Table 2). Among them acetate is the most important, occupying the first place among precursors (more than 75%).[17,23-29,32-35] Acetate is followed by carbon dioxide,[26-29,36-38] formate, methanol, [22,23,41] methylamines,[42] methylcobalamin,[17] and carbon monoxide.[17] According to the available data, no other carbon compounds support the growth of methane forming bacteria.

Table 2. Chemical reactions effected by methanogens.[54]

Chemical reaction	ΔG_0° relative to CH_4 kJ mol^{-1}
$CO_2+4H_2\rightarrow CH_4+2H_2O$	−139
$4HCOO^-+4H^+\rightarrow CH_4+2H_2O+3CO_2$	−119
$4CO+2H_2O\rightarrow CH_4+3CO_2$	−186
$CH_3COO^-+H^+\rightarrow CH_4+CO_2$	−31
$4CH_3OH\rightarrow 3CH_4+CO_2+2H_2O$	−103
$4CH_3NH_2+2H_2O\rightarrow 3CH_4+CO_2+2NH_3$	−75
$2(CH_3)_2NH+2H_2O\rightarrow 3CH_4+CO_2+2NH_3$	−74
$4(CH_3)_3N+6H_2O\rightarrow 9CH_4+3CO_2+4NH_3$	−75

Methanogenic bacteria convert 90–95% of the carbon used into methane in order to accumulate energy for constructive metabolism via the coupled generation of a transmembrane potential and only 5–10% of the carbon is converted into the biomass. By virtue of the above feature, up to 80–90% of the organic matter decomposed in the course of the development of the methanogenic consortium is converted into gas.[17]

In mixed cultures, methane-forming organisms can be readily determined with the aid of fluorescence microscopy:[43-44] they give rise to either a green fluorescence by virtue of the F_{420} factor or a blue fluoresence by virtue of 7-methylpterin[45] (see below).

Fairly important data have been obtained by investigating rRNA. It was found that methane-forming bacteria differ from all other organisms in terms of their 16S RNA nucleotide sequence.[46,47] In addition, methane-forming bacteria differ sharply from other organisms as regards the composition of the electron transferring agent as well as a series of coenzymes. The processes involved in their metabolisms also have characteristic features.[41,47]

On this basis and primarily as a result of the studies of the 16S rRNA, methane-forming bacteria are regarded as a special branch in the evolution of organisms and are classified as archebacteria.[46]

3. The Mechanisms of the Formation of Methane

The biosynthesis of methane is the main reaction leading to the generation of the energy necessary for the development of the cell. The universal scheme for the formation of methane by bacteria was first proposed in 1976 by Barker, who combined processes involving the biosynthesis of methane from H_2/CO_2, formate, acetate, and methanol:[48]

Since it had been shown even earlier that formate, formaldehyde, and methanol are not intermediates released into the culture medium in the course of the formation of methane from CO_2, the authors suggested that these C_1-compounds, reduced to different extents during their transformation into methane, should be linked to one or several compounds "X". Vigorous biochemical and physicochemical studies during the last 10–15 years made it possible to elucidate to an appreciable extent the nature of the compounds "X". In the first place, at least six unique coenzymes were isolated from methanogens and identified. These coenzymes are hardly encountered in other species of bacteria.

The compound

$$HS{-}CH_2{-}CH_2{-}SO_3^- \ .$$

which was called coenzyme M (CoM), was the first to be discovered and its involvement in the formation of methane was demonstrated. Coenzyme M can combine with a methyl group, being thereby converted into methyl coenzyme M ($CH_3SCH_2CH_2SO_3^-$). The latter plays a central role in the terminal stage of the formation of methane, which is associated with the demethylation of $CH_3-S-CoM$:[47]

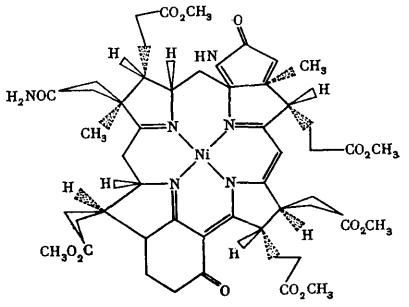
$$CH_3{-}S{-}CoM + 2H^+ + 2\bar{e} \xrightarrow[\text{methylcoenzyme M reductase}]{\text{comp. A, comp. B, } Mg^{2+}\text{, ATP}} CH_4 + HS{-}CoM \ .$$

This formally simple reaction is catalysed by an involved complex of enzymes and cofactors.[51] Component A is a protein complex exhibiting a hydrogenase activity. Four components were isolated from this complex: three proteins (A_1, A_2, and A_3) and the coenzyme FAD.[52] A_1 is an oxygen-resistant hydrogenase, which uses coenzyme F_{420} as the substrate. The hydrogenase A_1 may be identical with the F_{420}-reducing hydrogenase whose isolation has been described by Jacobson et al.[53] Compounds A_2 and A_3 are oxygen-labile proteins. It has been suggested that A_2 may participate in the reduction both at a formal level and as the activator methyl coenzyme M of the reductase system.[54] The function of A_3 is still not understood.

Component B is an oxygen-sensitive, thermally stable cofactor,[51] which has a molecular weight of about 1000 D and which contains an adenosine residue.[54] Catalytic amounts of ATP and Mg^{2+} are required for the functioning of the methyl coenzyme M reductase system. ATP probably activates enzymes or the coenzymes linked to the enzymes via acylation and phosphorylation reactions.[55]

Methyl coenzyme M reductase is an oxygen-stable protein consisting of three subunits and having a maximum absorption near 425 nm.[56] Two molecules of the recently discovered factor F_{430} function as prosthetic groups.[57]

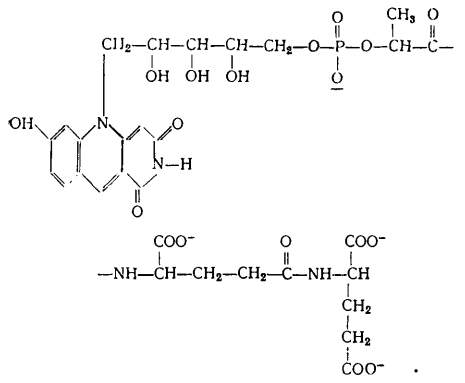
The factor F_{430}, given this name after the observation of its characteristic absorption maximum at 430 nm,[58] is a nickel-containing tetrapyrrole.[59–65] The structure of this chromophore, modified by methylating the carboxymethyl and carboxyethyl groups, has been established by Pfaltz et al.:[66]



The factor F_{430} usually forms ~1 : 1 complexes with coenzyme M and the complex is usually designated by $CoMF_{430}$.[67]

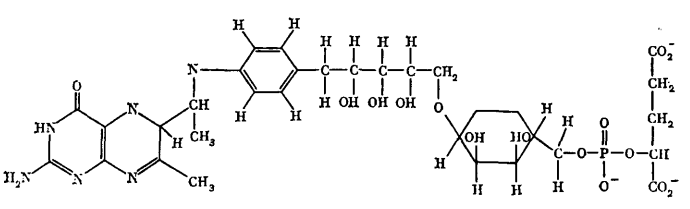
The function of $CoMF_{430}$ has not been ultimately established. From the chemical standpoint, this compound most probably functions as an electron transferring agent.[54]

The formation of methane from carbon dioxide represents the transfer of eight electrons from hydrogen to CO_2. Data obtained in the isotope fractionation of *M. thermoautotrophicum* have shown that H^+ from water is converted into methane, that H_2 serves solely as an electron donor, and that carbon dioxide is used in the gaseous form.[70,71] The coenzyme F_{420}, which has been given this designation on the basis of its fluorescence maximum in the oxidised form, first described in 1972 and having a low oxidation-reduction potential [E_0 = –0.34 V with respect to the normal hydrogen electrode (n.h.e.)], functions in this process as the electron transferring agent:[72–73]



This compound is the primary electron acceptor of hydrogenase,[39,53,53] formate dehydrogenase,[75–77] and F_{420}-dependent NADP-reductase[78] and is an electron donor in the terminal strage of the reduction of CO_2. Furthermore, F_{420} is an electron donor for two critical reactions in cell synthesis effected by pyruvate dehydrogenase and α-ketoglutarate dehydrogenase.

In 1978 experiments with labelled $^{14}CO_2$ showed that, over a period from 2 to 20 s, 25–50% of the label is bound into a compound giving rise to a bright yellow fluorescence.[36] These results suggested that the compound, later identified as 5,10-methenyl-5,6,7,8-tetrahydromethanopterin (5,10-methenyl-THF),[80] is an intermediate in the reduction of CO_2 to CH_4. After incubation under non-reducing conditions, 5,10-methenyl-THMP is converted into a compound which now exhibits a blue fluorescence and is a metabolic precursor of 5,10-methenyl-THMP (it does not contain the C_1 unit derived from CO_2). This compound has been called methanopterin.[81] Methanopterin has been isolated from the *Methanobacillus thermoautotrophicum* cells in 1983.[82] Its structure was determined in 1984 by high-resolution NMR spectroscopy (500 MHz)—by two dimensional ^1H and ^{13}C NMR:[83]

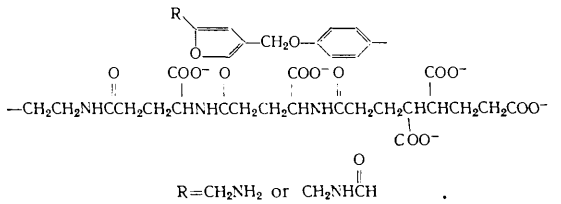


Methanosarcina barkeri contains another methanopterin derivative, which was called *sarcinapterin*. Its difference from methanopterin consists in the presence of glutamic acid joined to α-hydroxyglutaric acid.[81]

Brief incubation of the *M. thermoautotrophicum* cell suspension with $H^{13}CO_3^-$ (in a hydrogen atmosphere) and subsequent isolation of 5,10-methenyl-THMP showed that the label is present as the methenyl (=CH−) group.[54]

Thus methanopterin behaves as a C_1-transferring agent in two consecutive stages of the reduction of CO_2, which is manifested by the formation of methylene-THMP and methyl -THMP respectively.[54] These processes have been confirmed experimentally.[79,84]

Direct demonstration of the role of methanopterin in the reduction of CO_2 to methane has been achieved in a study[15] where it was shown that the absorption of CO_2 stimulated by coenzyme M and the so called RPG effect (see below) require the concerted action of two compounds stable with respect to oxygen and heating, one of which is methanopterin. The second compound, called the CDR-factor (the carbon dioxide reducing factor), was discovered in 1982 [86] and is yet another coenzyme in methanogens; the CDR-factor is encountered in two forms, namely as the free amine and as a formamide:



It has been suggested that in the latter case the formyl group originates in CO_2, since this form is in fact accumulated in the reaction mixture on incubation in an atmosphere of H_2 and CO_2 in the absence of methanopterin. This shows that the CDR-factor acts as a C_1-transferring agent before the THMP-derivative. Another name for the CDR-factor can also be encountered in the literature, namely methanofuran.[83] CO_2 is activated by the energy derived from ATP.[89] Reductive carboxylation is the energetically preferred type of CO_2 fixation.

The explanation of the socalled RPG effect, the sharp increase in the rate of reduction of CO_2 after the addition of $CH_2-S-CoM$ to the reaction mixture, is important.[90] This effect is produced also by a series of what are at first sight heterogeneous compounds: serine,[54] formaldehyde, hydroxymethylcoenzyme M,[91] pyruvate, L-ketoglutarate, L-malate, and isocitrate.[92] A common property of these compounds is that they can all function as donors of C_1-intermediates at different stages of the reduction process: of the formyl group (pyruvate, L-ketoglutarate, malate, and isocitrate), of the =CH− group (serine, formaldehyde, and hydroxymethylcoenzyme M), and of the methyl group ($CH_3-S-CoM$). Furthermore, the RPG effect clearly indicates a direct relation between the terminal (reduction of $CH_3-S-CoM$) and initial (activation of CO_2) stages of methanogenesis.[47,91]

Despite the fundamental correctness of the scheme proposed for methanogenesis by Barker, it is nevertheless too general in character. During the last 30 years, several attempts have been made to make this scheme more concrete,[46,48] but inadequate knowledge of the biochemistry of methanogens made it impossible to go outside the framework of general considerations and postulates. It was not until 1984 that Keltjens, having summarised the latest data, proposed a molecular model of the formation of methane from CO_2 and hydrogen.[54]

The basis of the Keltjens model is that CO_2 is activated by the methylreductase system (Fig.2). The one-electron reduction of the complex CH_3SCoMF_{430} leads to the formation of methane and a highly active thiyl radical, which activates and captures CO_2 with formation of a thiocarboxy-radical. The possibility of the existence of a thiyl radical in molecular methane-forming systems has been demonstrated experimentally.[69] The thiocarboxy-radical is subjected to attack by the CDR-radical coupled with one-electron reduction, which results in the formation of a complex of thiocarbamate, the CDR-factor, and $CoMF_{430}$ (Fig.2). Yet another one-electron reduction stage leads to the formation of the formamide form of the CDR-factor and the liberated thiyl radical. The subsequent stages involve the transfer of the formyl group of THMP and the formation of methyl-THMP. They take place with consumption of four electrons and the intermediate formation of methenyl- and methylene-THMP. Methyl-THMP is a relatively weak methylcarbonium (CH_3^+) donor. In order to be transferred to the thiyl radical, the CH_3^+ ion must be initially reduced to the methyl radical. This may be the function of component B of the methylcoenzyme M reductase system (Fig.2).

After the addition of the RPG-effectors, the increase in the degree of reduction of CO_2 is caused, as already mentioned, by the donation of C_1 units, which ultimately leads to an increase in the concentration of the thiyl radicals necessary for the binding of CO_2. However, the RPG-effect is transient apparently for two reasons: reaction of radical trapping agents and the exhaustion of the C_1 intermediates in the reduction of CO_2 for the synthesis of cell carbon.

Above we examined in detail the metabolism and biochemical characteristics of the methanogenic organisms specialising mainly in the conversion of H_2/CO_2 and/or formate. The metabolism and biochemical features of the organisms whose main substrates are acetate, methanol, and methylamines have been investigated to a much lesser extent, which can be explained both by the smaller number of organisms of this group and by certain methodological difficulties in their cultivation and investigation.[42,43] Hitherto it has been firmly established by the tracer atom method and certain other procedures that a common terminal methyl group transferring agent is coenzyme M for all methanogens.[36,50,93–96] It has been suggested that the primary recipients of the methyl group may be methanopterins or corrinoids, while the further transfer of the methyl group takes place as in the reduction of CO_2 with hydrogen.[93,97]

There exist two basic mechanisms of the transformation of acetate into methane and CO_2. The mechanism I, also referred to as the acetoclastic mechanism,[98,99] was described above and involves the cleavage of acetate in such a way that the methyl group is converted into methane and the carboxy-group is converted into CO_2. The mechanism II was proposed in 1936 by Barker and Van Neel and is a two-stage process.[100] Acetate initially decomposes to hydrogen and CO_2, which is then followed by the reduction of CO_2 with hydrogen. According to Van Neel's hypothesis, all the potential methanogenic substrates are initially converted into oxidised products and CO_2 and methane are formed as a result of the reduction of CO_2.[100] These two mechanisms can be differentiated using ^{14}C-labelled substrates.

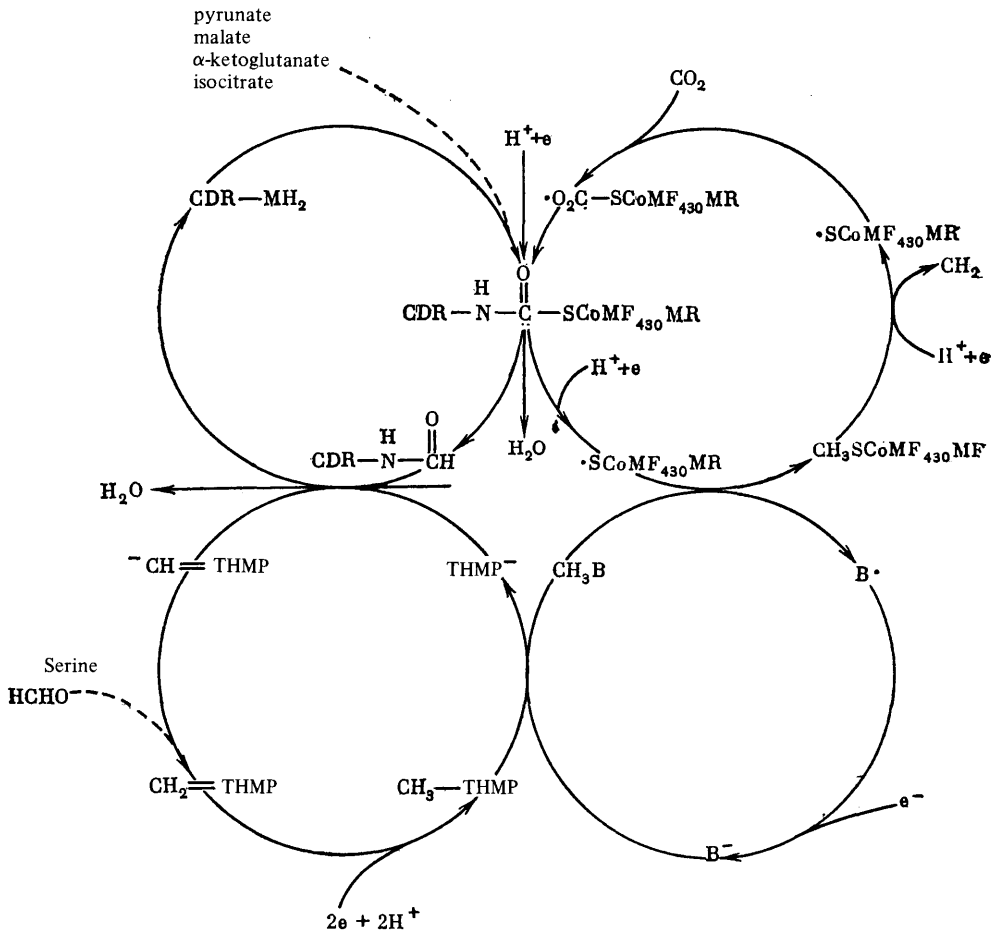


Figure 2. Keltjens molecular model for the reduction of CO_2 to methane.[54]

Numerous experiments have demonstrated that pure cultures belonging to the *Methanosarcina* family and also *Methanotrix soengenii* convert acetate via the mechanism I.[98,101,102] There is also no doubt that formate, methanol, and methylamines converted into methane by pure cultures of methanogens via the mechanism I.[46] Van Neel's hypothesis has been confirmed for other substrates, such as alcohols (C_2 and higher) and aliphatic acids (C_3 and higher), but subject to its significant modification which is that the conversion of these substrates takes place with participation of not one but several micro-organisms. The interaction of several micro-organisms takes place as a result of a process which has come to be called the interspecies hydrogen transfer.[103] This phenomenon was first demonstrated for an ethanol oxidising culture, the micro-organism called *Methanobacillus omelianskii*.[103] A similar interaction of cultures has been demonstrated in the methanogenic degradation of cellulose and hemicellulose,[21,104] glucose,[24–26,105] butyrate,[21,106,107] propionate,[108] acetate,[109] and also methanol, ethanol, and acetate by the methanogenic association of micro-organisms *Methanobacillus kuzneceovii*.[23–26,108,110] Interspecies hydrogen transfer is especially important in the anaerobic degradation of aliphatic acids, since their oxidation can proceed, for thermodynamic reasons, only at very low partial pressures of oxygen in the system, which is in fact ensured by the activity of hydrogen consuming organisms.[111–113]

Methanogens have played an enormous role in the genesis of natural gas on Earth. It has been demonstrated by geochemical analytical methods that more than 80% of gas deposits of industrial importance in the USSR consist of biological methane which has accumulated in such colossal amounts during billions of years of the activity of methanogens.[17] The advances in modern biotechnology permit the hope that in the near future it will be possible to replace a considerable proportion of the extracted natural gas by the industrial synthesis of methane.

4. Technological Principles of the Preparation of Biogas

The phenomenon of the evolution of combustible gas on decomposition of organic material under anaerobic conditions has been known for a long time. The first practical application of biogas dates back to the end of the XIXth century when in 1885 in the English city of Exeter methane obtained from a septic tank was used to illuminate streets.[114]

The first-scale factory for the manufacture of biogas was constructed in 1911 in Birmingham for the sterilisation of the solids from the sewage in that city. The methane formed was converted

into electrical energy. At the present time there exist a number of examples of the use of methane tanks in various countries of the World, this field of biotechnology passing through a period of intense development at the present time.[1,5,10,11,14]

The industrial preparation of biogas from organic waste has a number of advantages:[5]

(1) The heat generating capacity of biogas amounts to 20–28 MJ m^{-3} (0.7–0.8 kg of conventional fuel); the processing of 1 tonne of organic matter (dry weight) yields up to 800 m^3 of biogas.

(2) The process takes place periodically, semiperiodically, and continuously in large-scale reactors whose volume ranges from several cubic metres to thousands of cubic metres. The reactors are as a rule simple to construct.

(3) Methane fermentation achieves the effective purification of sewage and the processing of waste from animal husbandry and the cultivation of plants and of active sludge leads to the preparation of sterile high-quality fertilisers and to the complete mineralisation of nitrogen and phosphorus.

(4) The high coefficient of the conversion of the energy of organic substances into biogas, reaching 90%.

(5) Biogas can be used very effectively also directly as a fuel or can be converted with 83% efficiency into electrical and thermal energy by means of gas generators.

(6) In the anaerobic processing of waste, it is possible to obtain valuable biologically active compounds, for example, vitamin B_{12}, together with biogas.

A critical analysis of the economic problems associated with the introduction of biogas technology has been carried out.[115] It has been shown that the manufacture of biogas may be economically justified only when a series of conditions are observed: there must be a supply of raw materials with minimum and negligible transport and storage costs; there must exist a system for the utilisation of the gas without its accumulation and storage; there must exist a cheap source of low-potential heat for the heating and thermostatting of the methane tank.

Studies directed to the conversion into biogas of the waste from animal farms, which is regarded as an integral component part of modern animal farming industry, are of greatest practical interest.[116] The large-scale application of biogas technology makes it possible to solve in one process three inter-related problems—the preparation of a fuel, the conversion and sterilisation of waste, and the preparation of concentrated fertilisers.

An improved technology for the conversion of waste from the animal farming industry has been described.[117,120]

The rate-limiting stage in the preparation of biogas is the degradation of the biomass to oligomeric and monomeric components. Studies designed to intensify the depolymerisation processes by various methods are being prosecuted on these lines. One of the latest aspects of this field is associated with the use of ionising radiation. It has been shown that preliminary irradiation of biomass with γ-rays can intensify severalfold the methane formation process.[29,121]

Studies are being carried out on the automation and control of the methane generating process. For example, a correlation has been discovered between the productivity of the methane generator and the content of the coenzyme F_{420}. Methods have been developed for the determination of F_{420} in mixtures and procedures have been proposed for the estimation of the "methane generating force" of a mixed culture in terms of the content of coenzyme F_{420}.[123]

Fundamentally new possibilities in the biotechnology for the preparation of fuel are associated with the development of methods for the biogasification of peat.[124] Large deposits of peat fuel are known to exist in many countries, the development of their use being held back by the lack of an ecologically acceptable technology.

The first attempts to convert peat into biogas date back to the 1920's.[125] At the present time several projects designed to obtain biogas from peat are being developed. The project being developed by the Institute of Gas Technology (Chicago, USA), which has been called the "Biotherm Gas-process", provides for the combination of the conversion of peat into methane with participation of stages involving biological and thermochemical gasification.[126,127]

A second project, work on which is being carried out by the Dynatech Company (USA), provides for the chemical processing of peat with alkali coupled with an oxidative process and subsequent anaerobic conversion into biogas.[128,129]

The technical-economical parameters of various processes, including traditional processes have been compared and it has been shown that both projects may reach the stage of an economically significant technology in the immediate future. The main possibilities for the improvement of the technology are associated with the development of methods for the preliminary treatment of peat involving the improvement of its capacity for biodegradation.[124]

The rates of methane formation have been compared[130] for cellulose and hemicellulose in mesophilic and thermophilic decomposition processes. In the mesophilic process (35 °C), the degree of conversion of hemicellulose was higher than that of cellulose, but hemicellulose was converted significantly less effectively compared with cellulose under the conditions of thermophilic decomposition (55 °C). The rates of formation of gas from hemicellulose-containing materials are 0.3–0.6 of a volume of biogas per volume of the reactor per day for a methane content of 52–63% as a function of the process conditions.

The attempts to combine in a single system the generation of atomic energy and biogas are of great interest. There have been reports according to which a system for the preparation of biogas, based on the use of the heat of the cooling water, has been created within the framework of an atomic electric power station in Belgium. Algae converting biogas in the subsequent methanogenic stage have been cultivated using the low-potential discarded heat from the electric power station in water reservoirs.[131,132]

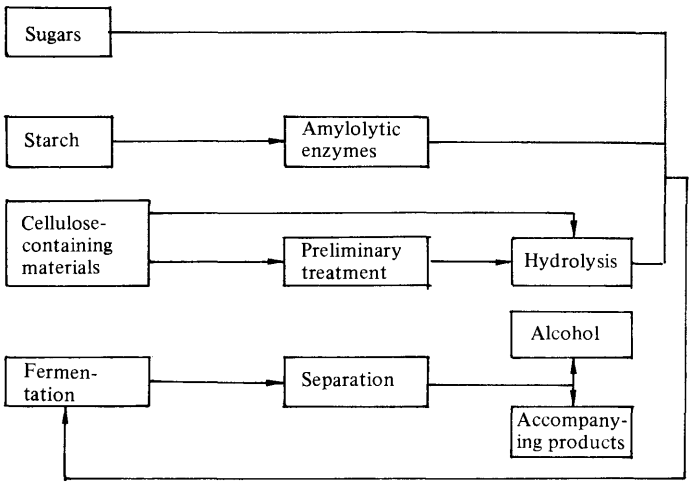
The present state of the biogas industry in the world has been surveyed in a number of reviews.[5,10,11]

III. ETHANOL

1. Chemical Principles of the Synthesis

With increasing deficiency of liquid mineral fuels, it has become necessary in many countries to replace petroleum by ethanol as a fuel, in the first place for the needs of automobile transport. The sources of raw material for the manufacture of fuel ethanol are plants with a high sugar content (sugar cane, sugar beet, etc.), starch (potatoes, maize, etc.), grain crops, as well as a wide variety of cheap plant materials of the lignocellulose type.

The biotechnological preparation of ethanol can be represented schematically as follows:



Only part of this scheme, based on the use of starch or sugars (molasses) as the initial raw material, has so far been realised on a wide scale. Low grade maize (corn) starch is thinned with α-amylase at a high temperature (80 °C, 20–30 min), hydrolysed with glucoamylase to soluble sugars (mainly glucose), and this is then followed by the yeast fermentation of glucose to ethanol, which is subsequently fractionally distilled.[133]

The rate-limiting stage in the conversion of the cheap cellulose-containing raw material is the hydrolysis stage (cellulose is approximately 100 times more difficult to hydrolyse than starch). At the present time, three principal methods of hydrolysis of cellulose are in the process of development and compete with one another: (1) with dilute inorganic (sulphuric) acids at a high temperature; (2) with concentrated inorganic acids (sulphuric, hydrochloric, or hydrofluoric acid) at a low temperature; (3) enzyme hydrolysis at a low temperature. Each method has definite advantages and disadvantages.

When concentrated acids are used, high rates of hydrolysis of cellulose are achieved, but problems associated with the recovery of the acids and the corrosion of the equipment arise.

Processes using dilute acids require high temperatures in order to attain technological rates of conversion of cellulose, but the rate of decomposition of glucose increases at the same time and equipment is again corroded.[143,144]

Enzyme hydrolysis does not suffer from the above disadvantages, but at the present time the cost of cellulases (enzymes hydrolysing cellulose) is fairly high. Furthermore, the attainment of high degrees of conversion of cellulose frequently requires an intense preliminary treatment to decompose the lignin shell and to convert cellulose from the crystalline to an amorphous state. Other problems in enzyme hydrolysis consist in the inhibition of cellulases by the hydrolysis products and in the inactivation of enzymes.

In general, hydrolysis with dilute acids makes it possible to achieve only 50–60% yields of glucose, while hydrolysis with concentrated acids or a multistage process involving the decrystallisation of cellulose (the Tsao–Purdue process) is potentially capable of reaching yields of 90%. The yield of glucose in enzyme hydrolysis depends greatly on the type of preliminary treatment (mechanical milling, delignification with solvents, treatment with live steam, preliminary hydrolysis of hemicelluloses with dilute acid) and can vary from less than 50% to more than 90%.[134–140]

Jones and Semrau[134] carried out an economic analysis of the cost of the final product (ethanol) for different methods of hydrolysis of cellulose. None of them has economic advantages, compared with the preparation of ethanol from grain, which has been traditional in the USA. However, the economic situation can change significantly if furfural, the principal side product of the acid hydrolysis of wood, becomes commercially significant as a chemical agent.[134]

The use of various component of the biomass not susceptible to alcohol fermentation is being studied in this connection. An interesting aspect of such research is associated with the development of methods of preparation of monomers from the biomass.[141,142] Thus a procedure has been described for the preparation of 2-vinylfuran—the component capable of serving as a basis for new polyvinyl polymers.

The use of a hybrid process, in which a dilute acid is employed for the preliminary treatment and separation of the corresponding fraction of wood (mainly the hemicellulose fraction), while enzymic hydrolysis is used to convert the residual cellulose into glucose, also appears very promising.[154]

Partial degradation of cellulose can likewise be achieved with the aid of a number of physical methods, for example, by treating cellulose with live steam or with γ-radiation. The effect on the enzyme and acid hydrolysis of the preliminary treatment [with radiation] of the biomass has been investigated and it has been shown that, for doses greater than 10 Mrad, bagasse (the residue from sugar cane after the juice has been pressed out) is degraded; bagasse irrigated with a dose of 100 Mrad affords 2–4 times more glucose than the non-irradiated specimen. Irradiation influences the acid hydrolysis to a greater extent than the enzyme hydrolysis.[145–147]

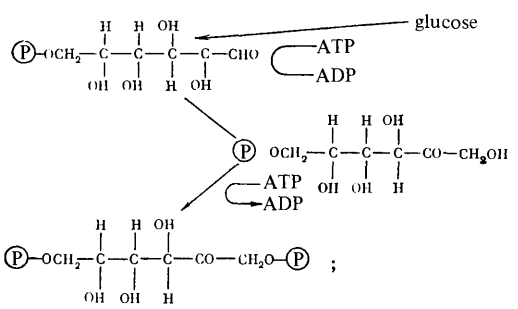
The second stage in the processing of cellulose—the conversion of carbohydrates into ethanol—is one of the oldest microbiological processes used by man:

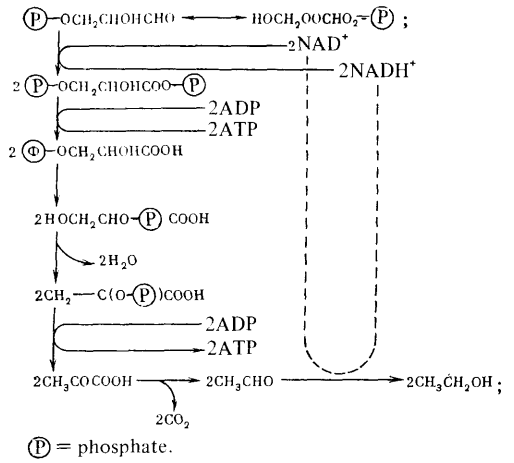
$$C_6H_{12}O_6 \rightleftharpoons 2C_2H_5OH + 2CO_2 .$$

The coefficient of the conversion of energy in this reaction is 98%.

The mechanism of the microbiological preparation of ethanol is fairly complex, but it has been investigated in great detail at the microbiological and biochemical levels[1] (see Scheme 1).

Scheme 1





(P) = phosphate.

On a technological scale, sugars are fermented to ethanol as a rule by yeast (*Candida brassicae, Candida utilis, Saccharomyces cerevisiae, etc.*). The theoretical yield of ethanol is 51 wt.% of the initial concentration of glucose, while the practical yield is 47 wt.% as a result of the growth of the yeast and the formation of side products. The inactivation of yeast by high concentrations of ethanol (in excess of 10–12%) creates many problems and for this reason methods for the extraction of ethanol from the culture medium are being vigorously developed.[148] In this sense, much hope is associated with the bacteria *Zymomonas mobilis* which ferments sugars twice as fast as yeast.[149] Thus the *Z. mobilis* cells immobilised in calcium alginate pellets afforded at the outlet from the reactor 102–116 g litre h^{-1} of ethanol for an incoming concentration of glucose of 200 g $litre^{-1}$.[150]

The idea of direct effectively single-stage conversion of polysaccharides into ethanol has gained wide currency in recent years. Thermophilic anaerobic bacteria are very promising in this connection: they do not require aeration, grow at high (60–65 °C) temperatures, grow rapidly on cellulose and exhibit a high metabolic activity, contain the complete set of enzymes of the cellulase complex, and ferment cellulose and sugars with formation of a limited spectrum of metabolites: ethanol, lactate, H_2, and CO_2.[137] These bacteria also have a number of advantages characteristic of thermophilic organisms in general. Thus at high temperatures there is, firstly, a decrease in the solubility of oxygen and other gases which lowers their toxic effect and increases the time during which anaerobic conditions are maintained, secondly, the viscosity of the solutions diminishes and the solubility of the substrates increases, which improves their accessibility to enzymes, and finally and thirdly, the volatility of ethanol increases, which permits its continuous distillation using a low vacuum, reducing thereby its inhibiting effect.

The technological application of thermophilic anaerobic bacteria is limited by a number of disadvantages: the lack of balance in the cellulase enzyme complex; the relatively low yield of ethanol to the fermented sugar molecule; the increased sensitivity to ethanol (as a rule their metabolism is almost completely suppressed already in the presence of 0.5% of ethanol in the medium); the low capacity to ferment the products of the hydrolysis of hemicelluloses.[137]

The natural strains of micro-organisms suitable for the direct conversion of plant raw material into ethanol require at the present time an improvement in their biological characteristics. This can be achieved by methods involving the selection of the appropriate mutants by the creation of recombinant strains with specified properties by genetic engineering and also by searching for new natural strains and by the selection of micro-organisms suitable for joint cultivation. The development of improved methods of preparation of ethanol, the creation of new strains of micro-organisms tolerant to an increased ethanol content and a low pH have been described.[152,153]

2. Technological Features and Economics

Brazil has the greatest experience in the use of ethanol as a fuel. The National Alcohol Programme (PROALCOOL), adopted by the Brazilian government in 1975, was the outcome of almost half a century's research in this field. The principal aim of this programme was to reduce the import of petroleum by partly replacing petrol by ethanol and made provision for the manufacture by 1985 of 107 billion litres of ethanol annually.[156] The source of alcohol was in this instance the fermentation of sugar obtained from sugar cane.[155] It is noteworthy that Brazil as a whole has successfully fulfilled these plans. The campaign conducted in that country in favour of replacing petrol by alcohol has enabled Brazil to save 2 billion dollars per year. The results of the Brazilian experiment for the development of systems for the preparation of fuel ethanol from sugar cane are described in a report by Khan and Fox.[157]

As already mentioned, the manufacture of ethanol from grain is the traditional procedure in the USA, the cost of such alcohol being 42 cents per litre.[134] The use of grain as the substrate is explained by the low prices and certain surpluses in the production of mainly maize grain.[157,158] These factors as well as the energy crisis led to the adoption in the USA of a national alcohol programme designed mainly to produce gasohol (90% of petrol and 10% of ethanol).[159] The popularity of this new fuel was due to its satisfactory anti-knocking properties (10–12% of ethanol is equivalent to 1–2 cm^3 of tetraethyl-lead per gallon)[159] and its economy—the consumption of gasohol is smaller by 25.3 g km^{-1} than that of non-ethylated petrol.[160]

Among the developments in the acid hydrolysis of lignocellulose materials, attention must be concentrated on the process developed at the New York University.[134] In order to obtain technologically acceptable rates of hydrolysis of wood by dilute sulphuric acid and in order to reduce the losses resulting from the decomposition of sugars at a high temperature, the process is carried out under continuous conditions with a short (10 s) residence time in the high-temperature zone in a specially designed reactor for a temperature of 232 °C and a pressure of 34.02 atm. Insoluble substances lignin, unreacted cellulose, ash components, and gypsum) are separated from the resulting suspension and the solution obtained, containing soluble sugars at a concentration of 10–11 wt.%, is supplied periodically into the reactor, where it is fermented to ethanol by yeast. The recycling time is 48 h. The concentration of ethanol at the outlet is 5.2 wt.% or 6.5 vol.%. The last stage is the distillation of ethanol.[134]

Economic calculations carried out for a factory with a productivity of 914.6 million litres of ethanol annually have shown that for an overall capital investment of about 132 million dollars the calculated cost of the ethanol would be 72 cents per litre. Thus it is seen from the calculation that the cost of the ethanol obtained by acid hydrolysis is fairly high and such technology cannot at present develop without government subsidies.

A group of scientists at the Michigan University have recently proposed a new process for the hydrolysis of wood with the aid of gaseous hydrogen fluoride. Dry wood is treated at a reduced pressure for 1 h. This results in the formation of glucosyl fluoride (up to

99% yield) from cellulose. Next, glucosyl fluoride is hydrolysed with water (1 h, 140 °C) with formation of glucose and hydrogen fluoride. The latter is recycled by evacuation or with the aid of slight heating and its residues in the solution are neutralised with calcium carbonate. The CaF_2 deposit is treated with sulphuric acid in order to achieve a more complete recyclisation of HF. The principal products of the process are glucose and lignin. The glucose is subsequently fermented to ethanol. The estimated cost of glucose is 12 cents per kilogram of which 7.5 cents represents the cost of the initial wood.[161] Unfortunately, there have been no communications so far about the scale of this process.

The entire wide variety of scientific and technological solutions of the problems concerning the enzymic conversion of cellulose into ethanol in the USA can be reduced to three basic processes.

(1) The use of separate reactors for the accumulation of cellulases, hydrolysis of cellulose, and the fermentation of sugars to ethanol (the Army Laboratory at Natick).

(2) The use of a separate reactor for the accumulation of cellulases and the combined process involving the conversion of cellulose into sugars and the fermentation of the sugars formed to alcohol (Gulf Oil Chemicals Co.—Arkansas State University).

(3) The use of a single reactor for the direct conversion of cellulose into ethanol with the aid of one or several species of microorganisms (Massachusets Institute of Technology).

The technology of the Gulf Oil Chemical Co. has been most thoroughly developed from the standpoint of technique and economics. Cellulose is hydrolysed by the cellulose enzymes of the fungus *Trichoderma reesei* and the sugars formed are fermented to ethanol by the cells of *Candida brassicae*.[135,162,163] It was proposed to scale up this technological process in three stages and a factory for the combined processing of 3000 tonnes of dry waste per day is to be built in the last stage, which is planned for the end of the 1980's. Apart from the production of 200 million litres of absolute alcohol annually, the factory will generate also 52.5 MW of electrical energy annually as a result of the combustion of the unused cellulose. The total cost of the planned factory is 230 million dollars. The commercial cost of the alcohol produced will be 58 cents per litre.[135]

The laboratory in Natick in collaboration with the New Brunswick Company constructed a pilot plant where wood is treated with steam and then hydrolysed by cellulases obtained by the deep culture of a mutant strain of *T. reesei* in a separate 400 litre fermenter. The sugars formed are fermented in a 250 litre reactor to give alcohol, which is distilled. The lignin and the unreacted cellulose are burnt. The apparatus has been automated to the highest possible extent for analysis and control.[134,164]

The process economics has been analysed for a factory with a productive capacity of 100 million litres of 95% ethanol annually, processing 495 000 of town waste containing 375 000 tonnes of cellulose. The capital investment in the construction of this factory is expected to be 83.5 million dollars and the intrinsic cost of ethanol is to be 42 cents.[135,164] According to other data, the intrinsic cost of ethanol from this process is 55 cents per litre.[134]

The process developed by the Massachusets Institute of Technology (MIT) is based on the employment of mutant strains of the thermophilic bacteria *C. thermocellum* and *C. thermosaccharolyticum* for the direct preparation of ethanol from agricultural cellulose-containing waste. In the laboratory experiments, the yield of alcohol reached 85%.[165] A disadvantage of this development is the relatively low rates of conversion of cellulose into ethanol. The economic analysis carried out was based on plans for a factory using the MIT technology processing 1500 tonnes of maize stems per day and capable of producing ~100 million litres of ethanol annually. The intrinsic cost of the ethanol is 28 cents per litre, while the cost of the raw material is 30 dollars per tonne. The capital outlay on the construction and operation of the factory is 34.4 million dollars.[135]

The Tsao–Purdue process is based on the preliminary treatment of cellulose-containing materials consisting in the dissolution of the cellulose fraction in cyclohexane, ethylenediamine, and concentrated phosphoric, sulphuric, and hydrochloric acids with subsequent precipitation of cellulose already in an amorphous form with methanol or water.[166] Recently the Tsao–Purdue process was criticised because of the considerable technical complexities in scaling up and is believed to be economically unfavourable.[135]

The Aietick Canadian Company developed an effective method for the preliminary treatment of lignocellulose materials for subsequent hydrolysis. Here Mason's method (or the co called steam explosion) is used, where live steam under pressure permeates into the biomass, whereupon the ordered structure of lignocellulose is broken down as a result of instantaneous decompression and then converted into a loose amorphous mass. The lignin then melts and can be readily separated from the cellulose fraction. Furthermore, such treatment results in the extraction of the hemicellulose fraction, which passes to water after the condensation of steam. Cellulose is hydrolysed by the enzyme preparations from *T. reesei* C-30 and *A. niger*. Under these conditions, 90–95% of cellulose and 80–85% of hemicellulose are converted into sugars in 100 h at 45–50 °C. The fermentation of the resulting glucose to ethanol takes place in 95% yield. The yield of ethanol is 270 litres from 1 tonne of wood. Xylose is not fermented by yeast and its concentrated solution serves after evaporation as a commercial product under the name "Feed molasses". If an effective fermentation of xylose to alcohol is also achieved, then the yield of ethanol may be 360 litres per tonne of wood. The lignin remaining after hydrolysis is used for the manufacture of phenol-formaldehyde plastics and adhesives.

Technical-economical calculations for the factory planned by the Aietick Company, designed to process 250 tonnes of lignocellulose daily with a productivity of 30 million litres of ethanol per year, have shown that the overall capital investment will be in the region of 10 million dollars and the cost of the ethanol will be 45 cents per litre.[133,135] One of the Canadian companies is planning to expand the factory in Manitoba which is already producing ethanol from barley by the Aietick process.

An analogous project has been developed by another Canadian firm—Stake Technology. Its difference from the Aietick process consists in the application of a continuous preliminary treatment of the lignocellulose raw material.[133,135]

The combined approach in Canada to the utilisation of biomass has also been manifested in the development of integrated agricultural projects including, for example, the growing of maize and the production of beef and fuel ethanol.[167]

The French government set aside in 1981 the sum of 26 million dollars for a programme designed to develop the manufacture of gasohol. It is proposed that the realisation of this programme by 1990 will enable France to satisfy the national requirements for transport fuel to the extent of 25–50%. It is planned to produce ethanol from wood, straw, and artichokes; the fermentation of the glucose syrups by immobilised cells will be combined with the removal of ethanol by extraction to prevent the inhibition of the process.[168]

In Japan interest in the preparation of ethanol from the biomass arose in the 1950's. Japanese technologists developed three processes for the hydrolysis of cellulose-containing raw material by concentrated acids at atmospheric pressure and a temperature not exceeding 100 °C.[169] Unfortunately the Japanese investigators were unable to eliminate fully the disadvantages characteristic of the hydrolysis by concentrated acids and more attention has been devoted to enzymic hydrolysis in the national project for the preparation of fuel ethanol, which has been executed by the Ministry of International Trade and Industry between 1980 and 1986. Japanese investigators have reported that they devised a very simple method for the enzymic conversion of cellulose-containing materials into sugars and the preparation of low cost sugars and ethanol with a considerable saving of energy.[135,155]

Scientific and technological activity in the development of processes for the preparation of fuel ethanol from biomass has also been manifested in India, Finland, Italy, Sweden, Austria, Australia, New Zealand, South Africa, Mauritius, and other countries.[114,170,171]

IV. THE ACETONE–BUTYL FERMENTATION

Interest in the preparation of organic solvents by a microbiological procedure has arisen anew recently. Examination of past history shows that interest in the acetone–butanol–ethanol fermentation waned and waxed anew, such interest determining the possibility of utilising the final fermentation products and also stimulating the research in this field.

The first major improvements in the process for the conversion of carbohydrates into butanol, acetone, and ethanol on an industrial scale were achieved during and after the First World War. The need for acetone was very high, which led to the rapid development of its manufacture. At the same time, butanol was not of much value and its storage and utilisation presented difficulties. However, after a time it was discovered that butanol is an extremely valuable chemical product and some of its esters came to be used in the manufacture of automobile varnishes and in other branches of industry.

It is essential to note that the USSR has been a pioneer in the development of the microbiological acetone-butyl industry, the scientific principles of which were developed by Academicians Shaposhnikov and Ierusalimskii.

The principal processes achieved on an industrial scale before the Second World War were the fermentation of the waste from the industrial manufacture of starch and molasses and the industrial processing of maize. Whether or not the industry was economical depended mainly on the cost of the raw material and after the Second World War the microbiological synthesis of solvents was abandoned in most countries as economically unfavourable in connection with the development of the production of synthetic solvents from cheap petroleum.[172,173]

The growing cost of the petroleum processing products during the 1970's stimulated the creation of more sophisticated technologies for the preparation of butanol. A commercially viable manufacturing process was developed on the basis of the fermentation of sugar cane molasses by a *C. acetobutylicum* culture.[174]

Butanol has effective characteristics as a fuel. By mixing up to 50% of butanol with petrol, a satisfactory fuel is produced.

The cultures used for the acetone–butanol fermentation consist of the *C. acetobutylicum* species and are distinguished, apart from morphogolical differences, also by the carbohydrate medium which they convert, by the rate of fermentation, by the type of nitrogen-containing nutrient substances required, and by the ratio of the solvents obtained.

The search for new strains is associated with the need to employ raw materials which are cheaper and more readily available than the expensive carbohydrates. The possibility of obtaining butanol from hydrolysed pine wood was investigated with the aid of *C.acetobutylicum* NC113-2951.[176] The fermentation was carried out at 30 °C for 5–7 days. The amount of hydrolysate obtained was 30 g litre^{-1} (4% of xylose, 6% of mannose, 2% of galactose, and 88% of glucose). The main hydrolysate was decolorised and steam-treated only in a combined process, which led to the removal of inhibitors and made it possible to obtain up to 1.6 g litre^{-1} of butanol which is equivalent to 90% of the yield of the product in relation to the carbohydrates adsorbed. However, during decolorisation the hydrolysates lost up to 30% of the sugars present. The use of a combination of cation- and anion-exchange resins for the purification of the hydrolysates made it possible to increase the yield of butanol as a result of subsequent fermentation (5.7 g litre^{-1} or 17% of the carbohydrates employed).

A *C. acetobutylicum* ATCC 324 culture was used to determine the optimum conditions for the preparation of butanol and acetone from acid buttermilk.[177] The culture of the above producer is capable of utilising several carbohydrates, including lactose, with formation of butanol, acetone, and ethanol in proportions of 6:3:1. The maximum synthesis of solvents was observed when sterile buttermilk was used in the fermenter without stirring. After 120 h, the pH fell to 5.2 and the concentration of solvents reached 9.2 g litre^{-1} and that of the residual lactic acid in the medium was 2.5 g litre^{-1}. Treatment in an autoclave and the absence of stirring increased the yield of solvents. Periodic fermentation of whey ultrafiltrate, glucose, lactose and galactose as carbon sources, by *C. beijerinckii* made it possible to compare the conditions for the preparation of butanol from the whey ultrafiltrate with those in its preparation from other substrates and to determine the optimum process parameters.[178]

The main aspects of the research on the improvement and reduction of the cost of the manufacture of butanol in our country involve the replacement of the expensive alimentary raw material (flour) by a non-alimentary raw material (for example sugar beet, molasses). Use of the *C. acetobuylicum*, strain S, culture, which made it possible to alter the solvent ratios and to obtain a fairly high yield of butanol (69–72%) for a content of residual sugar from 0.6 to 0.3%, is promising. The process terminates after 42 h, the content of the solvents at the end of the process amounting to 15.07 g litre^{-1} and including 11.03 g litre^{-1} of butanol, 3.38 g litre^{-1} of acetone, and 0.6 g litre^{-1} of ethanol.[179]

The utilisations of various sugars from hemicellulose hydrolysates by *C. acetobutylicum* have been compared.[177] A 90% yield of butanol can be observed in the fermentation of glucose. Five other sugars ensured the formation of butanol in decreasing amounts: cellobiose > mannose > arabinose > xylose > galactose.

An important problem involves the search for strains ultilising cellulose. It was found that only two out of 21 of the solvent producing *Clostridium* species strains tested exhibit a cellulolytic activity.[180] Furthermore, subsequent investigations revealed that the same strains exhibit endoglucanase and cellobiase activities, but their overall activity is insufficient for the hydrolysis of crystalline cellulose.

The biochemical principles of the anaerobic metabolism have been elucidated in fair detail and described in a number of studies.[181–183] *C. acetobutylicum* metabolises glucose to pyruvic acid via the

Embden–Meyerhof pathway with formation of two molecules of ATP and two molecules of NADP. Acetyl-CoA, CO_2, and H_2 are formed as a result of the phosphoroclastic pyruvate cleavage reaction. The amount of hydrogen in *C. acetobutylicum* varies as a function of the presence of NADH-ferredoxin oxidoreductase.[184] The acetyl-CoA formed is converted into acetate (ATP is synthesised), ethanol (two molecules of NADH are required), and acetoacetyl-CoA, which is either transformed into acetone or is reduced (two molecules of NADH are needed) to butyryl-CoA. *C. beijerinckii* reduces acetone to isopropyl alcohol.[185] It had been suggested earlier that the formation of butyrate is associated with transferase activity, but the latest studies have demonstrated that the main metabolic pathway proceeds via butyryl phosphate and the formation of ATP.[186,187] Butyryl-CoA is subsequently reduced to butanol with participation of two NADH molecules. The hydrogen, evolved in the first stages of the conversion of glucose, is consumed in the formation of NADH used to reduce the butanol.

It is known that in the course of the growth phase in the periodic cultivation of *C. acetobutylicum*, the main products are acetic and butyric acids, hydrogen, and CO_2. The acids are reassimilated when the cultivation pH falls and are converted into solvents with simultaneous consumption of the sugar. There exists the view that the accumulation of butyrate in the medium activates a new fermentation system, which leads to the formation of acetone and butanol and disturbs the usual mechanism of the cycle. The transition from the acid to the synthesis of the solvent can be partly accounted for by the latest enzymological studies at the level of the enzymes of these two phases. It has been shown that the activity of phosphate acetyltransferase and acetylkinase was greatly reduced and that of phosphate butyryltransferase vanished during the stage involving the synthesis of the solvent by *C. acetobutylicum* ATCC824.[187] A similar situation has been observed for *C. acetobutylicum* DS 14: the butyraldehyde and butanol dehydrogenase activities were determined only for cells synthesising the acetone–butanol mixture.[186] The same phenomenon has been observed for *C. beijerinckii*.[185] *C. acetobutylicum* possesses a transferase system which transfers the acetoacetyl-CoA from the cycle to the synthesis of acetoacetate and the latter can be decarboxylated to acteone. Acetate(butyrate):CoA transferase is an enzyme with a broad substrate specificity, which also exhibits a higher activity in the butanol synthesising cells than in the cells synthesising acid.[174,186] The decarboxylation of acetoacetate to acetone stimulates the transferase reaction via the well known acetoacetate decarboxylase, which is again induced only in the butanol synthesising cells.[174,186,187]

The synthesis of the reduced final products depends on the reducing potential of the cell. During the acid phase in the periodic culture portions of them are lost in the form of H_2. In the synthesis of the solvent, two moles of NADH are formed per mole of glucose and a certain amount of the former is also produced from the reduced ferredoxin. Consequently, in order to increase the amount of butanol, it is essential to increase the total amount of NADH. This can be achieved, for example, by inhibiting the hydrogenase at the acid formation stage[145] or via continuous cultivation in the solvent formation stage. The maximum theoretical yields from 1 g of glucose are 0.41 g of butanol, 0.32 g of acetone, and 0.5 g of ethanol. Thus, in the formation of a mixture of these products, the maximum theoretical yield depends on the product ratio. If this ratio is 6:3:1 (butanol–acetone–ethanol), which is typical, the maximum theoretical yield of solvents is 0.39 g g^{-1}.

It has been established that at a high pH mainly acids are synthesised whereas at a low pH an acetone–butanol mixture is formed. The optimum pH for the synthesis of solvents varies as a function of the strain and the cultivation conditions, lying as a rule in the range 4.0–6.0.[180,189] This is apparently associated with the fact that acetoacetate decarboxylase has a pH optimum in the region of 5.0.[190] Furthermore, the pH influences the ratio of the dissociated and undissociated forms of acetic and butyric acids and it is known that only the undissociated form permeates through the cell membrane.[191]

However, these conclusions cannot be applied to all the butanol synthesising *Clostridium* species. Significant synthesis of butanol by *C. beijerinckii* PI 13436 is attained at pH 6.8 and neither an acid concentration nor a pH which might be correlated with the onset of the formation of butanol were observed.[185] The synthesis of butanol by *C. acetobutylicum* NCIB 8052 (ATCC 824) can be induced at pH 7.0 by adding high concentrations of acetate and butyrate (100 mM each)[192] and in certain *C. acetobutylicum* cultures, isolated in Egypt, the final pH did not prevent the synthesis of butanol (20 g $litre^{-1}$) down to 6.4.[193] Whatever the process mechanism, the addition of acetate and butyrate to the periodic culture influences the time of the onset of synthesis,[185,192,194] the final product ratios, and the concentration and yield to an extent which cannot depend exclusively on the simple conversion of the acids into the acetone–butanol–ethanol mixture.[194]

An important factor in the formation of the acetone–butanol mixture is the concentration of the carbon source. Unduly low glucose concentrations[186,196,197] afforded as a result only acids. In a periodic culture, the organisms did not enter into the butanol formation phase under these conditions and in continuous systems the substrate concentration must be not less than 5 g $litre^{-1}$.[198]

Detailed studies of the kinetics of the formation of products were carried out by chemostatic cultivation with limiting glucose, nitrogen, and phosphate.[199] The specific rate of consumption of glucose increased with increase in the rate of dilution. An increase in the rate of dilution increased the rate of formation of acid, which did not appear at low rates of growth. A completely different picture obtained as regards the rate of formation of acetone, butanol, and ethanol. It has been shown that their amounts increase with increasing rate of dilution up to a certain point (0.1–0.2 h^{-1}) and then again decrease rapidly. Extrapolation indicates the formation of an acetone–butanol mixture at a zero rate of growth. Thus the synthesis of butanol is only partly associated with growth. If the butanol-synthesising cells are again placed in a buffer solution, they continue to synthesise the solvents. Thus non-growing cells can be used for the prolonged preparation of butanol.[198,200]

A weak point in acetone–butanol fermentation is the low concentration of the target products (about 2%). Solvents, especially butanol, are toxic to bacterial cells. In test experiments, the rate of growth of *C. acetobutylicum* ATCC 824 was 50% inhibited at a butanol concentration of 7–13 g $litre^{-1}$, an acetone concentration of 40 g $litre^{-1}$, and an ethanol concentration of 50–60 g $litre^{-1}$.[201] Complete growth inhibition was observed in the presence of 14–16 g $litre^{-1}$ of butanol and 70 g $litre^{-1}$ of acetone and ethanol. The lower concentration limit at which no decrease in the rate of growth takes place is 4.4–8 g $litre^{-1}$ of butanol. Other strains responded analogously to organic solvents and in certain cases they are even more sensitive than the strain 824. For a culture of *C. acetobutylicum* P 262, the addition of 10 g $litre^{-1}$ of butanol virtually stopped growth.

The difference between the inhibiting concentrations of the solvents can be accounted for by the differences in the hydrophobic properties of the alcohols.[202] The lipid layers in the cell membranes are acted upon by the solvents. It has been shown that butanol (0.5–1.5 vol.%), added to the lipid fraction obtained from cells in

the middle of the exponential phase of the growth of the *C. acetobutylicum* ATCC 824 strain, appreciably increases the mobility of the spin-labelled hydrocarbons in lipid dispersions or, in other words, butanol leads to the "thinning" of the lipid double layer.[203] It has been established that the composition of the lipid acyl chains changes, on passing from the exponential to the stationary growth phase to one with a higher percentage content of saturated chains. The addition of butanol (0.5–1 vol.%) to the cultures influences the composition of the chains in the same way. It has been concluded that the ability to increase the percentage content of saturated aliphatic acids in the membrane in response to the increase of the butanol level acts against the "thinning" effect of the latter.[203]

C. acetobutylicum is sensitive not only to butanol but also to acetic and butyric acids. The inhibiting effect by acids is correlated with the intercellular concentration of undissociated structures and with the pH.[204] A twofold decrease in the rate of growth occurs in the presence of 8–15 g litre^{-1} of acetic acid and 6–13 g litre^{-1} of butyric acid.[201]

At the present time, industrial fermentation with periodic cultivation has approached the limit of the biological possibilities of the cultures employed. For example, the Weisman strain of *C. acetobutylicum*, cultured in a 90 m^3 periodic fermenter on sugar cane molasses, affords an overall yield of solvent of 19.5 g litre^{-1} in the proprotions 6:3:1 (butanol–acetone–ethanol) after 30–34 h in 0.3 g g^{-1} yield and with a productivity of 0.6 g litre^{-1} h^{-1}. For comparison, we may note that the best result obtained on a laboratory apparatus with glucose as the source of carbon is as follows: overall yield of the acetone–butanol mixture 18.4–21.3 g litre^{-1} and a productivity of 0.3–0.9 g litre^{-1} h^{-1}.[205]

The change from periodic continuous cultivation regimes made it possible to increase the productivity in acetone–butanol fermentation. A two-stage chemostatic cultivation of *C. acetobutylicum* DS 1731, optimised with respect to pH and temperature, has been described.[199] The first stage was carried out at a rate of dilution D = 1.25 h^{-1} (37 °C, pH 4.3) and the second stage at D = 0.03 h^{-1} (33 °C, pH 4.3). The stream of synthetic medium contained 0.1 g litre^{-1} of KH_2PO_4 and 54 g litre^{-1} of glucose. These conditions permitted the complete utilisation of the carbon source, affording a yield of the final product of 18.2 g litre^{-1} [4.87:12.78:0.78 (g litre^{-1}) acetone–butanol–ethanol mixture].

Chemostatic cultivation of *C. acetobutylicum* ATCC 824 with glucose limitation (50 g litre^{-1}) and the use of a complex medium at D = 0.1 h^{-1} gave an overall solvent yield of 15.9 g litre^{-1} [5.4:9.5:1 (g litre^{-1} acetone–butanol–ethanol mixture]; a butanol yield of 0.32 g g^{-1} and a productivity of 2.56 g litre^{-1} h^{-1} were achieved at D = 0.22 h^{-1}. The high productivity of this system is associated with the high concentration of the biomass as a result of the employment of a complex medium. Evidently the productivity can be increased still further by recirculating the biomass.

The continuous formation of acetone and butanol can also be achieved by employing immobilised cells. In order to reduce the losses of activity, a technique designed to meter the neutrient substances has been developed.[198] Using this technique, the continuous production of an acetone–butanol mixture in the presence of *C. acetobutylicum* ATCC 824 cells immobilised on the calcium alginate gel or adsorbed on beechwood chippings has been achieved.[198] In the system with adsorbed cells, the best results were attained for D = 0.2 h^{-1}: the solvent yield was 6.3 g litre^{-1}, the butanol yield 0.33 g g^{-1}, and the productivity 1.2 g litre^{-1} h^{-1}. These are highly promising figures bearing in mind that the rate of growth of the micro-organisms was not raised to the maximum and the medium was not optimised.

The growing cells of *C.beijerinckii* MD 27.6 were immobilised in a calcium alginate gel for the continuous preparation of butanol and isopropyl alcohol. The medium contained glucose and a yeast extract. The best result was obtained for D = 0.3 h^{-1}: an overall solvent yield of 9–10 g litre^{-1} and a productivity 1.5 g litre^{-1} h^{-1}.

Thus, despite the fact that the acetone–butanol fermentation is one of the first purely microbiological processes developed at the industrial level, the renewal of interest in this manufacturing process can be justified only if a number of problems, capable of resulting in economically viable results, are solved. The use of an improved technology, such as continuous cultivation and immobilised cells, can increase the productivity of the fermentation. The attempts to solve the problem of the toxicity of butanol and acetone and to increase the yield of the products synthesised have been concentrated on the adaptation and selection of tolerant strains and also on the creation of various mutants in the study of the genetic control of the production of butanol. At the present time, studies have been published on the development of methods for genetic analysis which make it possible to manipulate the corresponding genes for the creation of strains capable of more productive synthesis of solvents and of altering their ratio .

It is noteworthy that the acetone–butyl fermentation is a waste-free industrial process. The carbon dioxide of hydrogen formed during fermentation can be regarded as secondary products. Carbon dioxide, liquid and solid, is used in the food industry and hydrogen is employed as a fuel or in methane formation processes. The liquid waste from industry containing riboflavin, vitamins, and protein is used as cattle feed.

V. HYDROGEN

An important natural phenomenon, which is of great interest from the standpoint of the conversion of energy, was discovered in 1942.[206] After adaptation to the dark, under anaerobic conditions, the cells of microscopic algae begin to evolve hydrogen vigorously in the course of several hours. Since the microscopic algae are capable of producing molecular oxygen in the light, there exists the possibility, in principle, of employing the mechanism of photosynthesis for the biophotolysis of water with conversion of light energy into a form of fuel.[1]

In recent years, the phenomenon involving the formation of hydrogen by microscopic algae has been investigated in a series of laboratories. The present state of this problem has been discussed in review articles.[1,2,206,207] There exist several examples of laboratory processes leading to the formation of hydrogen. The use of thermophilic algae *Mastigoladus laminosus* has been described.[208] The system for the formation of hydrogen acted in the course of several days with an efficiency in the utilisation of the energy of sunlight of 2.7%. The algal culture was projected against the action of oxygen with the aid of a mixture of argon, nitrogen, and CO_2.

The blue-green algae, exhibiting both hydrogenase and nitrogenase activities, are of interest in this sense. The limitation in the supply of nitrogen promotes the formation of hydrogen by a factor of 2.5–3.5 compared with the normal conditions.[133] The experiments performed with the blue-green algae *Anabaena cylindrica* showed that the yield of hydrogen increases by ~70% on periodic illumination (10 s period). An apparatus for the manufacture of

hydrogen has been created under laboratory conditions in which a suspension of algae circulated between dark and illuminated zones.[209]

The practical use of the phenomenon of the photoevolution of hydrogen by microscopic algae has not as yet been achieved in view of the low efficiency of the evolution of hydrogen under stationary conditions. It may be that further studies and the optimisation and increase in the process efficiency will create conditions for the technological exploitation of this phenomenon.

Experiments performed on photosynthesising bacteria have shown that the best candidates for the preparation of hydrogen are the purple bacteria and cyanobacteria. It has been reported that the use of immobilised cells of photosynthesising bacteria made it possible to achieve a productivity in the evolution of hydrogen of 40 ml H_2 per gramme of the dry cells per hour.[210] Fairly high productivities—180 ml H_2 from a litre of the culture medium per hour—have also been achieved by the continuous cultivation of the purple bacteria *Rhodospirillum rubrum* on a medium with lactate.[211]

At the end of the 1970's and the beginning of the 1980's, studies on artificial photosynthesis were also prosecuted vigorously.[1,68,76,213] Best results were attained on artificial systems containing illuminated chloroplasts and enzyme preparations of bacterial hydrogenases. Such systems were capable of evolving hydrogen at rates up to 94 μmol H_2 per milligramme of chlorophyll per hour in the course of several hours.[212]

The genetic modification of the photosynthesising organisms, the study of their biochemical pathways, the increase of the hydrogenase and nitrogenase activities, and the optimisation of the nutrition, illumination conditions, and immobilisation of micro-organisms are all ways leading to an increase in the efficiency of the photosynthesis and its industrial application.[133]

The ability of certain chemotropic organisms to evolve molecular hydrogen was also noted a fairly long time ago. Subsequently, this phenomenon was investigated in detail in our country and abroad. The present state of the problem has been analysed in detail.[79]

Hydrogen-forming micro-organisms are common in nature and hydrogen can be formed from carbohydrate compounds, including starch and cellulose and from aminoacids and ketoacids.

On complete decomposition of glucose solely to CO_2 and H_2, the limiting energy conversion efficiency of 99% can be achieved theoretically:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2,\ \Delta G_0' = -260\ \text{kJ mol}^{-1}.$$

In practice, under the conditions of clostridial fermentation the process proceeds with formation of acetate or acetate and butyrate apart from CO_2 and H_2:

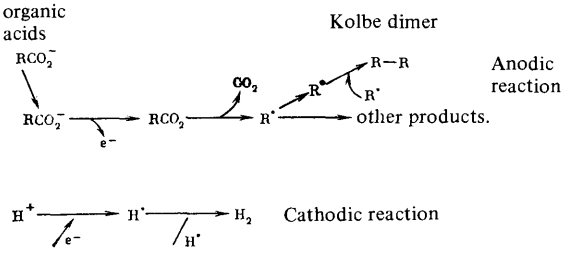
$$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2,$$
$$\Delta G_0' = -206{,}6\ \text{kJ mol}^{-1};$$
$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COO^- + 2HCO_3^- + 3H^+ + 2H_2,$$
$$\Delta G_0' = -255{,}2\ \text{kJ mol}^{-1}.$$

In the first case, 33% of the energy stored in glucose is converted into hydrogen form and in the second 16.7% is converted. This is determined by the fact that a considerable proportion of the energy remains in the aliphatic acids.[1] In order to increase the efficiency of the energy transformation, the aliphatic acids formed can be converted into fuel by the Kolbe electrolysis.[118] The process has been vigorously investigated by the Dynatech Company (USA).[133]

Organic acids are selectively extracted from the culture liquid by kerosine and are re-extracted with an aqueous solution. Organic acids are converted into liquid and gaseous fuel via the reaction

$$2CH_3CH_2CH_2COOH \rightarrow C_6H_{14} + 2CO_2 + H_2.$$

The fundamental anodic and cathodic reactions in the electrolysis are presented below:



The alkanes formed can serve as an effective fuel for internal combustion engines and the mixture of hydrogen and Co_2 produced is used for the generation of elecricity.

Anaerobic bacteria, which are capable of forming ethanol together with hydrogen, are also of definite interest. A new thermophilic hydrogen-forming culture, isolated in hydrothermal sources in Kamchatka, which decomposes glucose in accordance with the equation

$$C_6H_{12}O_6 + H_2O \rightarrow 2H_2 + 2CO_2 + C_2H_5OH + CH_3COOH,$$
$$\Delta G_0' = -201{,}44\ \text{kJ mol}^{-1},$$

has been described.[119] In this system the efficiency of the transformation of energy (of the overall energy into the hydrogen and ethanol forms) is 79%.

One of the latest advances in the preparation of hydrogen from water involves the creation of microbiological systems for the biophotolysis of water on the basis of cultrues of micro-organisms coupled via their metabolites.[122,175] Laboratory tests of a system for the photodecomposition of water into hydrogen and oxygen by sunlight with the separate formation of the gases have been carried out and completed. Productivities up to 0.5 litre H_2 per litre of the medium per hour (correspondingly 0.25 litre O_2 per lite of the medium per hour) have been obtained.[175]

In conclusion of this Section, one may note definite advances in laboratory studies of photobiological processes leading to the formation of hydrogen and also the creation of several demonstration plants. The scaling up of these processes still remains a complex biotechnological task, but the colossal advantages of the hydrogen power engineering inspire the hope that studies on these lines will continue and will bring about the expected practical results.

VI. CONCLUSION

The recent years have been characterised by an increasing interest in the development of renewable energy and raw material sources. Biotechnological processes occupy an important place in these projects. National programmes in fuel and biotechnology are being actively developed in the USA, Great Britain, France, Brazil, Japan, Canada, China, and other countries.

During the last ten years, studies on the utilisation of biosystems for the synthesis of fuel-type compounds with a high energy content have been carried out in a number of countries, including the USSR. These investigations have been directed towards the creation of a fundamentally new energy technology using renewable energy sources, in the first place solar energy.

At the present time two categories of systems capable of contributing significantly to the energy supply of the country are considered as likely prospects.

The first generation bioenergy technology presupposes the wide-scale industrial introduction of methanogenesis, which has now reached the level of technical solutions. The process represents anaerobic microbiological conversion of cellulose-containing materials into a mixture of methane and carbon dioxide. The quantitative characteristics of this process have not been investigated, the pathways leading to the transformation of the substances in a complex sequence of reactions have been studied, the key intermediates have been discovered, and a mathematical model and methods for the regulation of methanogenesis have been created for the first time.

The large-scale application of the biogas technology makes it possible to solve three inter-related problems—the preparation of the fuel, the concentration of organomineral fertilisers, and the problem of the protection of the environment against biological contamination (agricultural waste). By utilising the waste in the USSR alone, it should be possible to obtain up to 150 million tonnes of conventional fuel, which fully covers the future energy needs of agriculture.

At the present time agriculture consumes 60–62 million tonnes of petroleum products. By generating biogas, the agricultural industry can attain self-sufficiency in terms of energy.

The preparation of fuel ethanol and the acetone–butanol mixture from cellulose may make a significant contribution.

The second generation bioenergy technology is associated with the creation of a large-scale process for the biophotolysis of water—the reaction leading to the decomposition of water into hydrogen and oxygen by sunlight. At the present time, a reaction of this kind is achievable on the basis of microbiological cultures coupled via their intermediate compounds.

The complexities in the creation of systems for the transformation of solar energy involve the necessity to occupy large territories by technical constructions. Because of this, the constructions must be as simple as possible, should be convenient to use, and should not require expensive materials.

It has been suggested that biopower engineering plants will develop in the period 1990–2000, which will create a new power enginnering technology using high-energy and ecologically pure fuel. After sufficient development, processes of this category will meet a significant proportion of the energy needs of the community.

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The Influence of Surface Microstructures on the Physicochemical Properties of Oxides

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Published data on the role of defects and the microstructures formed on them in the chemistry of solid oxides have been examined. The conditions of formation, stability, and breakdown of the microstructures obtained on the external surface, at the phase boundaries, and in the inter-crystallite layers in polycrystalline solids have been described. It has been shown that surface compounds have an activating and an inhibiting action on the kinetics of solid-phase chemical reactions and on the thermomechanical and electrophysical properties of oxide materials.
The bibliography contains 74 references.

CONTENTS

I. Introduction 705
II. Methods for studying the surface and the inter-phase boundaries 706
III. The formation of the microstructures on defects in oxides containing an impurity, and their properties 707
IV. The relationship between the change in the defect character and the sequence of chemical reactions in mixtures of solid oxides 710
V. The mechanism of the action of impurities in sintering, and the deformational properties and thermal stability of oxide materials 712
VI. Surface microstructures and the protection of ceramic materials from reduction 714
VII. The influence of surface structures on the electrical properties of ceramic materials 714

I. INTRODUCTION

The study of surface microstructures is becoming one of the principal research fields in solid state chemistry and physics. All heterogeneous catalytic reactions take place on a surface, and progress in heterogeneous catalysis depends on the study of the composition, structure, and energetics of surface microstructures. The properties of metallic and non-metallic constructional materials are determined to a large extent by the phase boundaries and the grain boundaries, which are the most important structural elements. The study of the influence of defect microstructures (dislocations, grain boundaries, and phase boundaries) on the electronic processes in semiconductors is extremely important. Surface structures have an extremely marked influence on the kinetics of crystal growth and the habit and degree of perfection of crystals.

In the present review, published data on the role of surface microstructures in the physical chemistry of oxides have been systematised, and a critical analysis has been carried out. The dependence of the

properties of microstructures on the chemical character and concentration of impurities and on temperature, and the formation of non-equilibrium (intermediate) compounds in solid-phase chemical reactions as a consequence of the defect character of the structure, have been examined. Data on the influence of microstructures on the kinetics of the sintering of ceramic masses, the deformation of materials at high temperatures, and the electrophysical properties of doped oxides have been discussed.

II. METHODS FOR STUDYING THE SURFACE AND THE INTER-PHASE BOUNDARIES

Widely employed methods of analysis—chemical analysis, X-ray diffraction, spectroscopy, microscopy— do not give the required information on the properties of a surface and micro-volumes. The present section gives brief characteristics of some of the most informative methods for the analysis of a surface, the grain boundaries, and the phase boundaries in ceramic materials.

1. *X-Ray spectral microanalysis (XMA)* is based on the study of the X-ray emission spectra; the emission is excited in the specimen being analysed by an electron probe with a diameter of $0.7-1$ μm on the surface of the specimen. XMA can be used to determine all the elements from Li onward; the sensitivity is ~1 at.% for the light elements, and ~0.1 at.% for the middle and heavy elements. The spatial resolution is $1-3$ μm, because of the scattering of the exciting electron beam in the massive specimen. The thickness of the specimen is much greater than the mean free path of the electrons with an energy of $5-20$ keV usually employed in XMA.[1]

XMA can be used to carry out the local (within $1-3$ μm) qualitative and quantitative analysis of a substance with an accuracy of ~2 rel.%, to study the distribution of elements over the surface of a specimen, to study the reaction at a phase boundary, and to determine diffusion characteristics.

For XMA, the specimen should have a well polished surface, in order to observed its microstructure in a metallographic microscope and, which is more important, in order to carry out quantitative analysis, since the surface relief influences the intensity of the X-ray emission recorded. There are no restrictions on the electrophysical characteristics of the specimens.

2. *Scanning electron microscopy* makes it possible to study the topography of the surface of a specimen, its microstructure, and its domain structure in the case of ferromagnetics and ferroelectrics. When the back-reflected scattered electrons are recorded, the image produced gives information on the distribution of the elements on the surface of the specimen, particularly if the atomic number of the element concentrated at the grain boundaries differs considerably from that of the basic compound.[2] The attainable resolution is 10 nm.[3] The scanning electron microscope gives a resolution of ~1 μm when operating under X-ray microanalysis conditions.

3. *Scanning transmission electron microscopy (STEM)* can be used to study the microstructure and the morphology of the intergranular formations, and to determine the structure of phases by microdiffraction. The attainable spatial resolution is $\sim 3-5$ nm. A characteristic of STEM is that it is possible to carry out routine microanalysis with a spatial resolution of ~20 nm.[4,5] This high resolution is made possible by the use of electron beams with a field emission cathode, which make it possible to obtain an electron probe with a diameter $\leqslant 10$ nm on the surface of a specimen. Since STEM uses specimens whose thickness ($150-650$ nm) is smaller than the mean free path of the electrons in the specimen, the broadening of the beam in the specimen as a result of scattering is slight, and the diameter of the region analysed is $2-3$ times the diameter of the probe on the surface of the specimen.[6] The broadening also depends on the thickness of the specimen, the energy of the electron probe, and the characteristics of the target—atomic number, atomic mass, and density. Quantitative X-ray spectral analysis is difficult, so that the results of microanalysis by STEM must be regarded as only a qualitative demonstration of enrichment of the grain boundary.[5]

The preparation of specimens for STEM is tedious and complicated, since it is necessary to reduce the thickness of the specimen to ~100 nm. Chemical etching and etching by ion bombardment are used for this purpose. The preparation of the specimens may have a significant influence on the results, since in chemical etching, selective etching of different phases may take place, and in etching by ion bombardment, the atomisation of different elements is irregular[3] and the temperature of the specimen increases considerably, so that chemical reactions may take place with a change in the phase composition of the specimen. This must be borne in mind when discussing the results of microanalysis by STEM.

4. *Auger electron spectroscopy (AES)* is based on the analysis of the Auger electrons emitted by the specimen when it is irradiated by a beam of electrons with an energy of $1-3$ keV. The depth of removal of the Auger electrons varies from 0.4 nm to 3 nm, depending on their kinetic energy.[3] The AES data therefore carry information on the surface layer of the specimen.

AES makes it possible to determine the qualitative and approximate quantitative composition of the surface (all elements except H and He); its sensitivity corresponds to $\sim 10^{-2}$ monolayer. Under scanning conditions it is possible to study the distribution of the elements over the surface of the specimen; the spatial resolution in this case is determined by the diameter of the exciting beam of electrons, and is usually $5-20$ μm. The most interesting feature is the possibility of observing the Auger spectra directly during the ion etching of the specimen; this makes it possible to obtain the distribution of elements along the depth and to obtain information on the reactions taking place in the region of a phase interface. No special preparation of the specimens is required; in the study of dielectrics, difficulties are encountered, associated with the charging of the surface.

5. *X-Ray photoelectron spectroscopy (XPES)* or electron spectroscopy for chemical analysis (ESCA) is based on the analysis of the photoelectrons emitted by the specimen when it is irradiated by a monochromatic beam of X-rays. The depth of removal of the photoelectrons is several nanometres, that is spatial ESCA, like AES, carries information about the surface of the specimen. XPES has no spatial resolution over the surface, since it is extremely difficult to focus the X-ray beam to a diameter smaller than 1 mm.

XPES makes it possible to carry out the qualitative and quantitative analysis of a surface and to determine all the elements of the periodic system with a sensitivity of ~0.1 at.% (for uniform distribution of the element being determined) and an uncertainty of not more than 10 rel.%.

A significant advantage of XPES is the simplicity of quantitative analysis, since there is no inter-element influence in the determination of any elements. Special preparation of the specimens is not required, and there are no restrictions on the electrophysical properties of the specimens. The methods are more informative when XPES and AES are used together.

6. *Secondary ion mass spectroscopy (SIMS)* is based on the analysis of the secondary ions emitted by a target when it is bombarded by a beam of primary ions with an energy of 1–20 keV. The secondary ion mass spectrum contains differently charged monatomic ions of the main substance, the ions of polyatomic clusters, and the ions of impurities and chemical compounds, and the interpretation of the mass spectrum is tedious. A significant advantage of SIMS over other methods is its high sensitivity, from 10^{-7} at.% to 10^{-9} at.%.

The recording of the mass spectra with constant etching of the surface of the specimen makes it possible to obtain the distribution of the elements being determined along the thickness of the surface layer; the resolution along the layer (with allowance for the physical factors restricting the resolution—the roughness of the surface, the formation of etching facets or cones, and atomic mixing) is ~10 nm.

In the ion micro-probe, in the study of the distribution of elements over the surface of the specimen, the spatial resolution is determined by the size of the ion probe (1–10 μm). Preliminary preparation of the specimens is not required. The analysis of dielectrics is difficult, because of charging of the surface.

7. *Autoradiography (ARG)* is based on the recording of the distribution of a radioactive isotope in the specimen being studied from the blackening of photoemulsion applied to the specimen (or a photographic plate), under the influence of nuclear radiation. For contact radiography, the spatial resolution is ~20 μm, and for radiography with applied emulsions combined with electron microscopy the resolution is ~1 μm. ARG gives information on the diffusion characteristics of the phase boundaries and grain boundaries.[7] Any material can be studied by autoradiography. The restrictions are related to the selection of a radioactive isotope of the element being studied, suitable for radiography.

A detailed comparative analysis of methods for studying a surface has been given in a published review.[8]

III. THE FORMATION OF THE MICROSTRUCTURES ON DEFECTS IN OXIDES CONTAINING AN IMPURITY, AND THEIR PROPERTIES

Natural minerals and oxides used in technology contain non-controlled impurities or specially intoduced additives (mineralisers, activators, modifiers), which form microstructures as a result of internal adsorption on defects. Table 1 gives the compositions of microstructures in oxides, determined by XPES and using electron and ion micro-probes.

X-Ray electron studies of polycrystalline oxides[9] containing small quantities of impurity (0.01–1 mole %) showed that in the specimens $MgO-[Al_2O_3]$, $SnO_2-[CaO]$, $TiO_2-[CaO]$, and $TiO_2-[BaO]$, the compounds $MgAl_2O_4$,[9–12] $CaSnO_3$,[14] $CaTiO_3$, and $BaTiO_3$ [9] respectively are formed as local microstructures in the region of the defects. The synthesis temperature was 1650–1800 K. The composition of the surface was determined from the integral intensity of the analytical lines $Mg2s_{1/2}$, $Ca2p_{3/2}$, $Ba3d_{5/2}$, $Al2s_{1/2}$, $Ti2p_{3/2}$, and $Sn3d_{5/2}$ with allowance for the photo-ionisation cross-sections.[27]

The results of an X-ray electron study of the polycrystalline oxide MgO containing small quantities of added Al_2O_3 are given in Fig.1.[10] With increase in the Al_2O_3 concentration from 0.4 mole % to 2 mole % in the surface layer there was a decrease in the concentration of Mg in octahedral coordinatoin [binding energy E_b(Mg. $2s_{1/2}$) = 87.5 eV], indicating the formation of spinel $MgAl_2O_4$.

Table 1. The formation of microstructures on defects containing impurities (0.01–1 mole %).

Oxide	Impurity	Microstructure	Refs.
MgO	Al_2O_3	$MgAl_2O_4$	[9–11]
Al_2O_3	MgO	$MgAl_2O_4$	[12]
Al_2O_3	Ln_2O_3*	$LnAlO_3$	[13]
SnO_2	CaO	$CaSnO_3$	[9, 14]
SnO_2	TiO_2	TiO_2 in SnO_2**	[9, 15]
SnO_2	ZnO	ZnO in SnO_2**	[9, 16]
SnO_2	NiO	NiO in SnO_2**	[9, 16]
SnO_2	Nb_2O_5	Nb_2O_5 in SnO_2**	[9, 16]
ZrO_2	CaO	$CaZrO_3$, $CaZr_4O_9$	[9, 17, 18]
ZrO_2	Y_2O_3	Y_2O_3 in ZrO_2**	[9, 19]
Al_2O_3	NiO	$NiAl_2O_4$	[9, 12]
Cr_2O_3	CrO_3	$xCr_2^{III}O_3 \cdot yCr^{VI}O_3$	[9, 20, 21]
Cr_2O_3	La_2O_3	$La_2(CrO_4)_3$	[9, 20, 22]
MgO	NiO	NiO in MgO**	[9]
TiO_2	SnO_2	SnO_2 in TiO_2**	[15]
SnO_2	SiO_2	eutectic	[15]
Nb_2O_5	BaO	$BaNb_6O_{16}$ in Nb_2O_5**	[23]
Ta_2O_5	Nb_2O_5	Nb_2O_5 in Ta_2O_5**	[23]
$BaTiO_3$	$SrTiO_3$	$SrTiO_3$ in $BaTiO_3$**	[23]
$CaTiO_3$	CaO	Ca_3TiO_5	[24]
TiO_2	Ta_2O_5	$TiTaO_4$ in TiO_2**	[25]
CoO	Cr_2O_3	$CoCr_2O_4$	[26]
CeO_2	La_2O_3	$mLa_2O_3 \cdot nCeO_{2-x}$	[10]
TiO_2	CaO	$CaTiO_3$	[9]
TiO_2	BaO	$BaTiO_3$	[9]
Al_2O_3	Y_2O_3	$Y_4Al_2O_9$, $YAlO_3$	[9]

*Ln = La, Ce, Pr, Nd.
**Solid solutions.

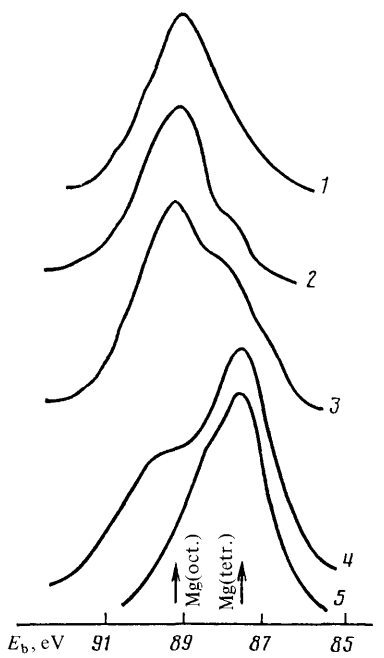


Figure 1. Mg2*s* X-ray electron spectra: *1*) MgO, *2–4*) MgO containing 0.4, 0.8, and 2.0 mole % Al_2O_3 respectively, *5*) $MgAl_2O_4$ (spinel).[10]

The ratio Al/Mg in the surface layer with a thickness of ~8.0 nm, found from the intensities of the Mg and Al lines, is 0.3, whereas in spinel, Al/Mg = 2. This lack of agreement is apparently due to the formation of spinel as local inclusions in an MgO matrix both along the depth of the layer and over the surface of the specimen, and the observed value of the Al/Mg ratio is the averaged value. Electron-microscope studies[11] showed that the formation of spinel involves the accumulation of crystals with dimensions of 0.5–10 μm, distributed in disordered fashion in the surface layer.

The dependence of the surface formations in a CeO_2 ceramic on the concentration of added La_2O_3 has been studied experimentally.[10] The $Ce3d_{5/2}$ spectrum in CeO_2 has characteristic lines with E_b = 882.3 eV and E_b = 882.6 eV. When CeO_2 contains added La_2O_3, a new $Ce3d_{5/2}$ line appears, with E_b = 381.3 eV, which can be assigned to a surface compound. The enrichment in La_2O_3 of a surface layer with a thickness of 8–10 nm, established from the intensities of the Ce and La lines, corresponds to an approximately five-fold increase in the La_2O_3 concentration relative to the average value for the specimen. In the surface film with a thickness of several atomic layers (1–1.5 nm), the La_2O_3 concentration is probably even greater, as a result of chemisorption. With increase in the La_2O_3 concentration, the line due to the new compound becomes stronger, and the lines with E_b = 882.3 eV and 882.6 eV become weaker. These data indicate that the introduction of La_2O_3 into CeO_2 leads to the formation on the surface of the CeO_2 granules of a micro-phase in which the states of the Ce atoms differ significantly from their states in CeO_2. According to the equilibrium diagram of the $CeO_2-La_2O_3$ system,[28] CeO_2 and La_2O_3 form restricted solid solutions. No chemical compounds are formed in this system. Thus in the $CeO_2-La_2O_3$ system, the chemistry of the surface micro-phases differs from the chemistry of the macro-phases. The compound formed was not identified.

Table 1 shows that, on the defects, microstructures are formed as chemical compounds which have been identified in the equilibrium diagrams ($MgAl_2O_4$, $CaTiO_3$, etc.)[9] or as compounds which are unstable in macro-volumes, for example $La_2(Cr^{VI}O_4)_3$.[9,20] In the systems with restricted solid solutions $SnO_2-Nb_2O_5$, SnO_2-NiO, SnO_2-ZnO,[9,16] and SnO_2-TiO_2, the micro-phases and the macro-phases differ in the concentration of the dissolved component.[9,15] The microstructures may be produced on the surface, and also along the boundaries of crystals and blocks and on dislocations, that is in the zones in which defects are concentrated. The crystallographic properties of the main oxide and the impurity play an important role in the formation of microstructures. The distribution coefficients of the impurities vary over a wide range, and depend on the concentration of the impurity, the nature of the interaction between the impurity and the defects of the matrix, and on temperature.

X-Ray electron spectroscopy has been used[12] to study a specimen of aluminium oxide containing 0.06 mole % MgO and 0.002 mole % CaO. The concentrations of the impurities determined along the grain boundaries were 0.2 mole % MgO and 3.4 mole % CaO, corresponding to enrichment coefficients $K = [MgO]_{boundary}/[MgO]_{bulk}$ = 3.3 and $K = [CaO]_{boundary}/[CaO]_{bulk}$ = 1700. Magnesium oxide forms surface microstructures consisting of non-stoichiometric spinel in the form of isolated units, whereas calcium oxide is distributed uniformly along the boundaries and is concentrated in several atomic layers of the surface of the crystals. A decrease in the segregation of calcium oxide is observed with increase in temperature.

In titanium oxide specimens containing added barium oxide,[9] the surface layer with a thickness of 8–10 nm was enriched in barium oxide; with increase in the concentration of the additive in the specimen, although its concentration in the surface layer increased, the distribution coefficient K decreased. In the surface layers, BaO was present as local formations with the composition $BaTiO_3$.

In the SnO_2-CaO system, the compounds $CaSnO_3$ and Ca_2SnO_4 are formed.[29] Quantitative X-ray electron analysis of the surface showed that the coefficient of enrichment of the surface layer of the specimens in calcium oxide reached 520 at a CaO additive concentration of 0.01 mole %, and 7.8 at a CaO concentration of 10 mole %.[30] In the surface layer, the tin is present as tin(IV) in an octahedral environment of oxygen atoms [SnO_6; $E_b(Sn3d_{5/2})$ = 486.7 eV], as in SnO_2. The Ca atoms have cubo-octahedral coordination, similar to that observed in $CaSnO_3$. For $CaSnO_3$ and $CaTiO_3$, $E_b(Ca2p_{3/2})$ = 347.2 eV; for CaO with calcium in octahedral coordination, the value is 346.3 eV. The $Ca2p_{3/2}$ spectrum of the compound Ca_2SnO_4, which contains calcium ions in two non-equivalent positions, is the superposition of the spectra of $CaTiO_3$ and CaO. Thus the coordination of the Ca atoms changes from octahedral in CaO to cubo-octahedral in $CaSnO_3$. Moreover, XPES data obtained with a positive charge on the surface showed that the specimens with a low CaO concentration contain two phases in the surface layer—SnO_2 (continuous layer) and $CaSnO_3$ (local formations).

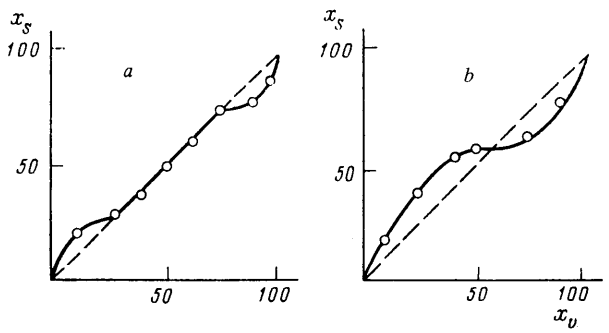


Figure 2. Composition of the surface layer of specimens in the SnO_2-TiO_2 system at different heating temperatures: *a*) 1373 K, *b*) 1673 K; x_v and x_s are the volume and surface concentrations of TiO_2.[15]

The SnO_2-TiO_2 system[15] is characterised by much smaller surface enrichment coefficients than the SnO_2-CaO system. At a concentration of 0.1 mole % TiO_2 in tin(IV) oxide, the enrichment coefficient is 11, and with the addition of 0.1 mole % SnO_2 to the TiO_2 matrix the coefficient is 50. Fig.2 gives the dependence of the composition of the surface of the specimen on its bulk composition in the SnO_2-TiO_2 system. At a heating temperature of 1373 K in the range of bulk compositions 25–75 mole % TiO_2, the surface layer is two-phase, and its composition corresponds exactly to that of the macro-volume. In the regions adjoining the pure components of the system, the surface layer is single-phase, and its composition differs from that of the bulk. Increase in the heating temperature to 1673 K leads to the formation, throughout the entire composition range, of a single-phase surface layer, whose composition differs from that of the bulk. Thus in this system, surface solid solutions TiO_2-SnO_2 are formed, and the range of their existence is broader than that for the bulk phases.

The distribution of added SiO_2 in polycrystalline SnO_2 is characterised by the following parameters.[15] With change in the quantity of added SiO_2 from 0.1 mole % to 5.0 mole %, the enrichment coefficient changes from 320 to 12. The coordination numbers of tin and silicon remain unchanged. The surface layer of the specimens is two-phase throughout the composition range.

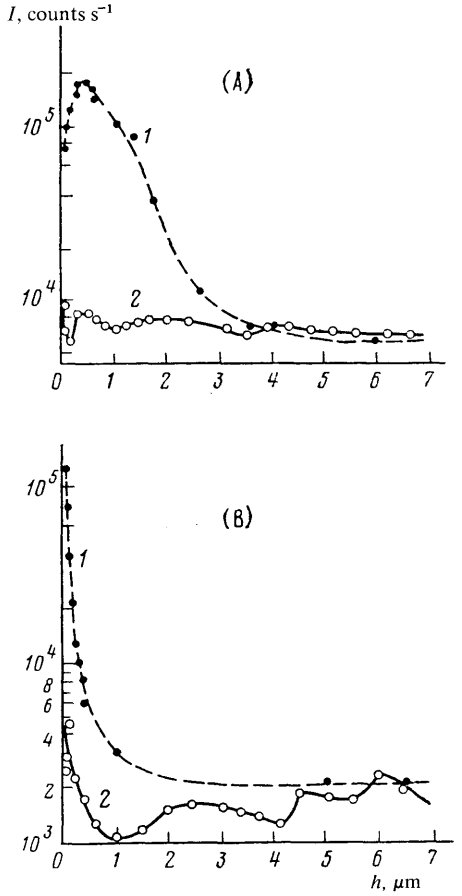


Figure 3. Mass-spectrometric microanalysis of the distribution of Al in slowly cooled (*1*) and quenched (*2*) MgO specimens containing 0.187 mass % Al (*A*) and 0.006 mass % Al (*B*); *h* is the depth of the layer analysed, *I* is the number of counts in 1 s, ^{27}Al.[11]

If the impurity forms continuous solid solutions with the oxide matrix (isomorphous systems), the internal adsorption of the isomorphous impurity is slight, $K \simeq 1$. The compounds NiO and MgO form a continuous series of solid solutions.[29] An XPES analysis of polycrystalline magnesium containing NiO showed that the concentration of nickel oxide in the surface layer is practically the same as that in the bulk.[9] The $Ni2p_{3/2}$ and $Mg2s_{1/2}$ binding energies in the surface layer of the specimen are the same as in the pure oxides. This indicates that solid solutions of NiO in MgO are formed both in the surface layer and in the bulk.

The stability and concentration of the microstructures on the defects change with change in temperature. The dependence of the surface segregation of Al_2O_3 in MgO on the thermal treatment conditions has been studied.[11] Single crystals of magnesium oxide containing 0.187 mass % and 0.006 mass % Al in solid solution [specimens (A) and (B) respectively] were heated in air for several hours at a temperature of 2073 K. Half of the specimens were subjected to air quenching by ejection from the furnace, and the rest were cooled in the furnace over a period of several hours. The results of the experiments are given in Fig.3. In the specimen cooled slowly (A), the maximum concentration of Al was established at a depth of less than 1 μm from the surface. Microscope and mass-spectrometric analyses showed the formation of local inclusions of spinel in the surface layers. The quenched specimen showed little change in the concentration of aluminium in the layer next to the surface, and no heterogeneous formations were detected. At high temperatures, desorption and solution of Al_2O_3 in the bulk of the MgO crystal take place. On slow cooling, segregation of Al_2O_3 developed on the defects, and the formation of microstructures with the composition $MgAl_2O_4$ was observed. Similar processes took place in the (B) specimens. Comparison of the curves for specimens (A) and (B) shows that the depth of formation of the microstructures increases with increase in the concentration of impurity.

The kinetics of the segregation of Al_2O_3 on the defects in an MgO matrix have been studied.[31] The rate of separation of Al_2O_3 from the $MgO-Al_2O_3$ solid solution and the formation of spinel along the grain boundaries increase with increase in the concentration of the dissolved component. The process is controlled by diffusion.

Table 2. Primary products of the chemical reaction in oxide mixtures.

Systems	Primary products	*A*	Refs.
$MgO-Al_2O_3$	$MgAl_2O_4$	1:1, 1:13	[34]
$CaO-Al_2O_3$	$CaAl_2O_4$	3:1, 12:7, 1:1, 1:2, 1:6	[34]
$SrO-Al_2O_3$	$SrAl_2O_4$	3:1, 2:1, 1:1, 1:2, 1:6	[34]
$BaO-Al_2O_3$	$BaAl_2O_4$	3:1, 2:1, 1:1, 1:6	[34]
$CaO-Fe_2O_3$	$Ca_2Fe_2O_5$	2:1, 1:1, 1:2	[34]
$MgO-SiO_2$	Mg_2SiO_4	2:1, 1:1	[34]
$CaO-SiO_2$	Ca_2SiO_4	3:1, 2:1, 3:2, 1:1	[34]
$CrO-SiO_2$	Sr_2SiO_4	2:1, 1:1	[34]
$BaO-SiO_2$	Ba_2SiO_4	2:1, 1:1, 2:3	[34]
$MgO-TiO_2$	$MgTiO_3$	2:1, 1:1, 1:2	[34]
$CaO-TiO_2$	$CaTiO_3$	3:1, 2:1, 1:1	[34]
$BaO-TiO_2$	$BaTiO_3$	1:1, 1:2, 1:3, 1:4	[34]
$PbO-MoO_3$	$PbMoO_4$	2:1, 1:1	[34]
$PbO-WO_3$	$PbWO_4$	2:1, 1:1	[34]
$Y_2O_3-Al_2O_3$	$Y_4Al_2O_9$, $YAlO_3$	2:1, 1:1, 3:5	[22, 35, 37]
$Y_2O_3-Fe_2O_3$	$YFeO_3$	1:1, 3:5	[22]
$*Ln_2O_3-Fe_2O_3$	$LnFeO_3$	1:1, 3:5	[22]
$Ln_2O_3-Al_2O_3$	$LnAlO_3$	1:1, 1:11	[13]
$CaO-SnO_2$	$CaSnO_3$	2:1, 1:1	[14, 34]
$CaO-ZrO_2$	$CaZrO_3$, $CaZr_4O_9$	1:1, 1:4**	[17, 18]
$La_2O_3-Cr_2O_3$	$La_2(CrO_4)_3$	1:1	[21, 22]

Note. *A* is the molar ratio of the oxides in the final products.

*Ln = La, Ce, Pr, Nd.

**Solid solution based on ZrO_2.

An X-ray electron study[9,14] of polycrystalline tin(IV) oxide containing small quantities of added calcium oxide showed that the surface layer with a thickness of 8–10 nm is enriched in calcium oxide; the enrichment coefficient *K* reached values of 520 and 7.8 for concentrations of the additive of 0.01 mole % and 10 mole %

respectively. The surface was two-phase; the SnO_2 matrix contained local formations of $CaSnO_3$. The formation of the surface layer and its stability at high temperatures were studied. The surface layer was removed by grinding. The specimens were heated to different temperatures, kept for 1 h, and then subjected to air quenching to preserve the distribution of the additive, established at the given temperature. After each thermal treatment, the spectra of the surface of the specimen were recorded, and their intensities were used to calculate the Ca/Sn ratio. At low heating temperatures with treatment for 1 h, the surface structure did not form at all. The maximum segregation (Ca/Sn = 0.53) wa attained at 1773 K. At higher temperatures, the reverse process, that is the solution of the microstructure in the matrix, took place.

The depth (thickness) of the surface formations in crystalline oxides varies over a wide range and depends on the nature and concentration of the impurities present in the surface structures. Fig.3 shows that the boundaries of the surface formations, facing into the crystals, have an indistinct "diffuse" form. With increase in the concentration of impurity, the depth of segregation increases. The depth of segregation of the impurities at the grain boundaries also depends on temperature, and increases with increase in the latter.[32]

The surface and the grain boundaries of oxides have an electric charge, as a consequence of the presence of an excess of ions of a given sign.[32] This surface charge is compensated by ions of opposite sign, which are formed close to the surface and extend to a depth of 2–10 nm.

IV. THE RELATIONSHIP BETWEEN THE CHANGE IN THE DEFECT CHARACTER AND THE SEQUENCE OF CHEMICAL REACTIONS IN MIXTURES OF SOLID OXIDES

Solid-phase reactions generally take place in several stages. Irrespective of the reagent ratio in the original mixture, the intermediate reaction product is a definite compound.[13,17,22,34–37] Examples of these reactions are given in Table 2.

It has been suggested[34] that the compound with the highest crystallisation temperature is formed first. This rule is not confirmed by a number of reactions, however. For example, in mCaO + $n$$Al_2O_2$, mMgO + $n$$TiO_2$, and $m$$Y_2O_3$ + $n$$Al_2O_3$ mixtures, irrespective of the component ratio, the compounds $CaAl_2O_4$, $MgTiO_3$, and $YAlO_3$ respectively are formed in the first stage of the reaction. According to the equilibrium diagrams of the $CaO-Al_2O_3$, $MgO-TiO_2$, and $Y_2O_3-Al_2O_3$ systems,[29] the compounds formed first are not the most refractory. The physicochemical factors causing solid-phase reactions to take place in stages have been studied.[20]

Comparison of the formation of microstructures in oxides containing impurities (Table 1) and the primary reaction products of the corresponding oxides in solid-phase reactions (Table 2) shows that defects play a definite role in these processes. In reacting oxide mixtures, the compounds formed first are those which are also produced on defects in the oxides.[20] For example, in mMgO + $n$$Al_2O_3$, mCaO + $n$$SnO_2$, mCaO + $n$$TiO_2$, and mBaO + $n$$TiO_2$ mixtures, irrespective of the component ratio, the compounds $MgAl_2O_4$, $CaSnO_3$, $CaTiO_3$, and $BaTiO_3$ respectively are formed first. On the other hand, in the same systems, but at concentrations of the second components from 0.01 mole % to 1 mole % (see Table 1), the compounds $MgAl_2O_4$, $CaSnO_3$, $CaTiO_3$, and $BaTiO_3$ respectively are formed as local microstructures on defects.

In a 2CaO + SnO_2 mixture at temperatures of 1200–1500 K, reactions take place to give the primary product $CaSnO_3$, and when the reaction mixture contains sufficient calcium oxide, this product reacts further with it to give the compound Ca_2SnO_4.[34]

Solid-phase chemical reactions are accompanied by a change in the defect character of the reacting mixture. According to Ref.34, the chemical reaction involves a number of elementary processes: covering of the surface, breakdown of the crystals and disordering as a result of surface and bulk diffusion, actual chemical reaction, an increase in the specific surface of the reacting substances, subsequent formation of a defect crystalline product, and removal of the defects in the crystal lattice of the compound formed. At definite stages, these processes lead to an increase and then a decrease in the defect character of the reacting mixture.

In the synthesis of compounds with the garnet structure $A_3B_5O_{12}$, where A = Ln, Y, and B = Al, Fe, the solid-phase reactions in the $3A_2O_3$ + $5B_2O_3$ mixtures take place with the formation of monoclinic $Y_4Al_2O_9$ and cubic $YAlO_3$ as intermediate products.[22,36] For this reason, it is difficult to obtain the pure product $A_3B_5O_{12}$.

An X-ray electron spectroscopic study[20] of the synthesised compound $Y_3Al_5O_{12}$ in the surface layer of a specimen with a thickness of 7–10 nm established the ratio Y/Al = 1.03 ± 0.05, which corresponds to the compound $YAlO_3$. The $Al2s_{1/2}$ binding energy in the surface layer is 119.2 ± 0.1 eV. In the compounds $YAlO_3$ and $LaAlO_3$, aluminium is in octahedral coordination, $E_b(Al2s_{1/2})$ = 119.3 ± 0.1 eV. For aluminium in tetrahedral coordination in sodalite $3NaAlSiO_4.NaCl$, E_b = 118.2 ± 0.1 eV. In the garnet structure, Al occupies tetrahedral positions. On the surface of the specimen with the composition $Y_3Al_5O_{12}$, aluminium was detected in octahedral coordination. The composition of the surface and the octahedral coordination of aluminium indicate that microstructures of the compound $YAlO_3$ are formed in the defect surface layer of the specimen with the composition $Y_3Al_5O_{12}$. $YAlO_3$ microstructures may also be produced along the boundaries of the crystals and blocks and on dislocations, that is in the zones where defects are concentrated. Thus in the $3Y_2O_3$ + $5Al_2O_3$ reaction mixture, the intermediate compounds $YAlO_3$ and $Y_4Al_2O_9$ are formed in the initial period of intensive defect formation.

In the systems given in Table 2, the intermediate reaction products of the oxides are generally found on the corresponding equilibrium diagrams. The formation on defects of new microstructures with compositions and structures differing from those of the equilibrium compounds is also possible, however. An example is provided by the $Cr_2O_3-La_2O_3$ system.

In an La_2O_3 + Cr_2O_3 mixture at a temperature of 873 K, phases corresponding to the chromate $La_2(CrO_4)_3$ and the chromite $LaCrO_3$ were detected in addition to the original oxides[20,22] (Fig.4). The kinetic curve *3* (the formation of the intermediate chromate) has a maximum indicating the predominant formation of chromate in the initial stage of the reaction of chromium(VI) according to the scheme

$$1.5Cr_2O_3 + 2.25O_2 + La_2O_3 \rightarrow La_2(CrO_4)_3.$$

The course of curve *3* is determined by two factors: the change in the defect character of the reaction mixture, which is responsible for the production of the maximum, and the presence of lanthanum oxide, which binds Cr^{VI} in a chemical compound.[20]

XPES has established the formation of metastable microstructures $xCr_2O_3.yCrO_3$ on defects in a Cr_2O_3 matrix,[38] the concentration of which decreases with increase in temperature and with decrease in

the oxygen pressure in the gaseous medium.[21] Metastable microstructures influence the reactivity and catalytic activity of substances, and the sintering and recrystallisation of solids.[10,16,20,21,39]

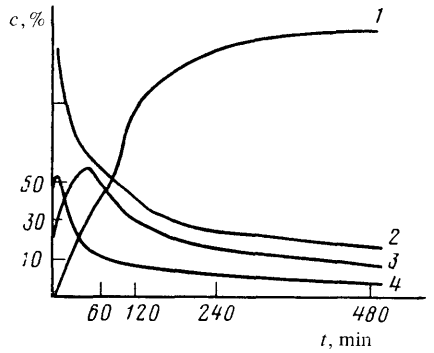


Figure 4. Kinetics of the reactions in an $La_2O_3 + Cr_2O_3$ mixture in air at 873 K; *c* is the concentration: *1*) $LaCrO_3$, *2*) La_2O_3, *3*) $La_2.(CrO_4)_3$, *4*) Cr_2O_3.[20,22]

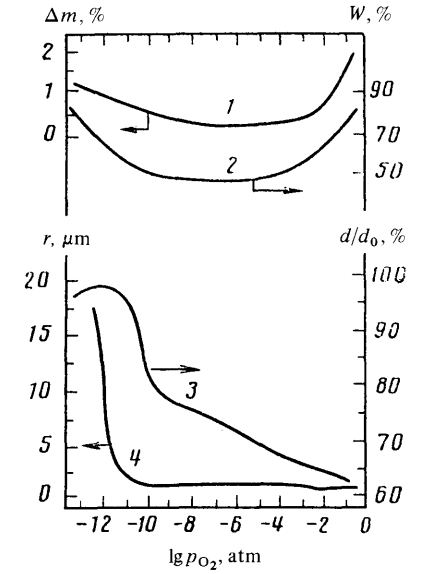


Figure 5. Change in the volatility, reactivity, sintering, and collective recrystallisation of chromium oxide on the partial pressure of oxygen:[21] *1*) mass loss (Δm) after 1 h at 1870 K;[40] *2*) quantity (*W*) of bound chromium oxide formed by the reaction $MgO + Cr_2O_3 = MgCr_2O_4$ after 1 h at 1620 K;[21] *3*) relative density (d/d_0) of chromium oxide specimens, sintering at 1870 K, 1 h;[40,41] *4*) size of the crystals (*r*), heating at 1970 K for 1 h.[21]

The results of studies[21,40–42] of the dependnece of the properties of chromium oxide and its compounds on the partial pressure of oxygen are given in Fig.5. The most intensive mass loss by a specimen of chromium oxide at a temperature of 1873 K (curve *1* in Fig.5) takes place at an oxygen pressure of 1 atm. This high volatility is due to the following features. At increased temperatures, chemical adsorption of oxygen on Cr_2O_3 crystals takes place,[21,43] to give oxygen-containing surface compounds of chromium with an increased valence $CrO_{1.5+x}$ (CrO_3, CrO_2), which are highly volatile. With decrease in the partial pressure of oxygen, the volatility of the specimens decreases. In the oxygen pressure range $10^{-3}-10^{-5}$ atm, the surface compounds $CrO_{1.5+x}$ become unstable, and their concentration decreases, and with further decrease in p_{O_2} they may may not be formed.

At low partial pressures of oxygen ($10^{-10}-10^{-13}$ atm), the volatility of the specimens increases again. Under these conditions, chromium oxide dissociates on the surface of the particles according to the scheme

$$^2/_3Cr_2O_3 \rightleftarrows {}^4/_3Cr + O_2 .$$

The rate of the reaction $MgO + Cr_2O_3 \rightarrow MgCr_2O_4$ (curve *2*) and the volatility of chromium oxide (curve *1*) change in the same sense with change in the partial pressure of oxygen. The activating factors in these processes are, firstly, the formation of the surface compounds $CrO_{1.5+x}$ at a high oxygen pressure of $10^{-2}-1$ atm, and, secondly, the predissociation of Cr_2O_3 at a low oxygen pressure of $10^{-10}-10^{-13}$ atm.

The rates of the sintering (curve *3*) and collective recrystallisation (curve *4*) of chromium oxide in oxygen (1 atm) and in air are reduced considerably. After heating at temperatures of 1870–2020 K for 1 h in the gaseous media indicated, the specimens remain porous and finely crystalline. Intensive sintering and crystal growth begin at oxygen pressures of $10^{-10}-10^{-11}$ atm and $10^{-11}-10^{-12}$ atm respectively. This effect of the surface compound $CrO_{1.5+x}$ is determined by the thermodynamic conditions on the surface of the particles. The formation of $MgCr_2O_4$ from the oxides at 1273 K takes place with $\Delta H = -10.3$ kcal and $\Delta G = -8.1$ kcal mole^{-1}.[21] The heats of sintering of the oxides are apparently comparable with the heats of the change from the amorphous to the crystalline state (1–3 kcal mole^{-1} [21]). The heats of collective recrystallisation are probably of the same order of magnitude as the energies of polymorphic transformations (0.01–1 kcal mole^{-1} [21]). The heat of adsorption of oxygen on the surface of chromium oxide, calculated from the equilibrium isobar, is 3.7 kcal mole^{-1}.[21]

The suppression of the sintering and recrystallisation of chromium oxide by adsorbed oxygen ($p = 1$ atm) is possible if ΔG_0, that is the thermodynamic potential of the formation of the surface compound $CrO_{1.5+x}$, is greater than the thermodynamic potential of the sintering or collective recrystallisation (ΔG_s) of chromium oxide: $\Delta G_a > \Delta G_s$, where ΔG_a relates to the adsorption of oxygen (here, the absolute values of the thermodynamic potentials are understood). The thermodynamically more stable surface compound prevents the decrease in the surface which takes place on sintering and collective recrystallisation. If the partial pressure of oxygen is lowered to values at which $\Delta G_a < \Delta G_s$, intensive sintering and recrystallisation of chromium oxide begin, as observed experimentally. The activation of the formation of chromium spinel at $p_{O_2} = 1$ atm is due to the fact that $\Delta G_0 > \Delta G_a$. The higher activity of the surface compound $CrO_{1.5+x}$ is due to the fact that its dissociation pressure is higher than that of Cr_2O_3. The dissociative activation of the surface compound reaches a maximum value at thermodynamic equilibrium, that is on fulfilment of the condition $\Delta G = RT \ln(p_{O_2}/p^*) = 0$, where p^* is the dissociation pressure of the surface compound $CrO_{1.5+x}$.

In the high-temperature synthesis of oxide materials, the water vapour which is always present in the furnace atmosphere is adsorbed on the oxide particles and activates the physicochemical processes taking place. A study[4] of the influence of the presence of oxygen and water vapour on the kinetics of the reactions of the oxides MgO, CaO, BaO, and ZnO with Al_2O_3 and of CaO with quartz and amorphous silica showed that at increased temperatures in an oxygen atmosphere and more particularly in the presence of water vapour the oxides are more reactive than in a vacuum. The surface complexes formed, MO_{n+x} or $MO_n.xH_2O$, activate crystallisation and sintering and increase the reactivity of the material.[44]

V. THE MECHANISM OF THE ACTION OF IMPURITIES IN SINTERING, AND THE DEFORMATIONAL PROPERTIES AND THERMAL STABILITY OF OXIDE MATERIALS

The mechanism of the activating and inhibiting action of impurities on physicochemical processes in solids is not completely clear, and a single theory has not been developed. The most widely accepted model is that in which disorder is produced in the lattice of the matrix by ions with a different valence as a result of a change in the concentration of vacancies in the anion or cation sublattices. Many experimental data are difficult to explain using this model, however.

As shown in sections III and IV of the present review, impurities react with defects of the matrix and in micro-volumes to form compounds differing in their composition, structure, and energy from the defect-free regions of the matrix. Thus real solids are microheterogeneous systems. To investigate the mechanisms of the processes taking place in these systems, it is necessary to study the chemical composition, structure, and energy state of the formations in local micro-volumes.

The effect of added Ln_2O_3 (Ln = lanthanide) on the kinetics of the sintering of cerium oxide has been studied.[10,13,45] According to the equilibrium diagrams,[13,29] these oxides in the concentration range 0–10 mole % Ln_2O_3 studied react with cerium oxide to form solid solutions with the fluorite structure. The results of experiments to study the influence of added lanthanum oxide on the shrinkage of cerium oxide are given in Fig.6. The Ln_2O_3 impurity forms a chemical compound on the defects of the CeO_2 matrix (see Table 1). The formation of the microstructure should pass through a stage involving the formation of a eutectic, depending on the concentration of the additive.

In the primary sintering of mechanical mixtures of the powders (curve *1* in Fig.6), when the additives have not yet penetrated into the cerium oxide particles, the effective concentration of the additive on the surface of the cerium oxide particles is much greater than that corresponding to its final (equilibrium) distribution (curves *2* and *3* in Fig.6), and the critical state of the microstructures is produced at a lower actual concentration of the additive (0.5 mole % Ln_2O_3). On the second and third heating of the specimens (curves *2* and *3* in Fig.6), the maximum intensities of sintering correspond to an additive concentration of 1.25 mole % Ln_2O_3. With further increase in the additive concentration of 1.25 mole % Ln_2O_3. With further increase in the additive concentration (> 1.25 mole %), a decrease in the rate of sintering is observed, and the additive acts as an inhibitor (range of the stable state of the microstructures). With increase in the sintering temperature to 1873 K, the shrinkage maximum becomes flatter, and at 1923 K the additive activates the sintering throughout the concentration range studied. As shown in section III, the stability and concentration of the microstructures changes with change in temperature. At 1923 K, the microstructures "dissolve" in the CeO_2 matrix.

The results of experiments[45] to study the influence of single (Sm_2O_3) and combined (Sm_2O_3 + Gd_2O_3) and (Sm_2O_3 + Gd_2O_3 + Y_2O_3) additives on the sintering of cerium oxide show that the effect of the added mixtures is additive, since the valences are the same, and the structures of the electron levels and the ion dimensions are similar: $R(Sm^{3+})$ = 0.97 Å, $R(Gd^{3+})$ = 0.94 Å, $R(Y^{3+})$ = 0.97 Å.[45] In the mixtures containing (98 – *x*) mole % CeO_2 + 2 mole % La_2O_3 + *x* mole % Sm_2O_3, increase in the samarium oxide concentration is accompanied by a regular decrease in the shrinkage of the cerium oxide specimens. The reason for this behaviour of the mixtures is that lanthanum oxide forms more stable microstructures than samarium oxide. The change in the shrinkage when the complex additives La_2O_3 + Y_2O_3(Sm_2O_3) are used[45] is similar to that when only lanthanum oxide is added. Preferential internal adsorption of lanthanum oxide apparently takes place as a result of the higher energy of interaction with the defects of the matrix for lanthanum ions compared with yttrium or samarium ions.

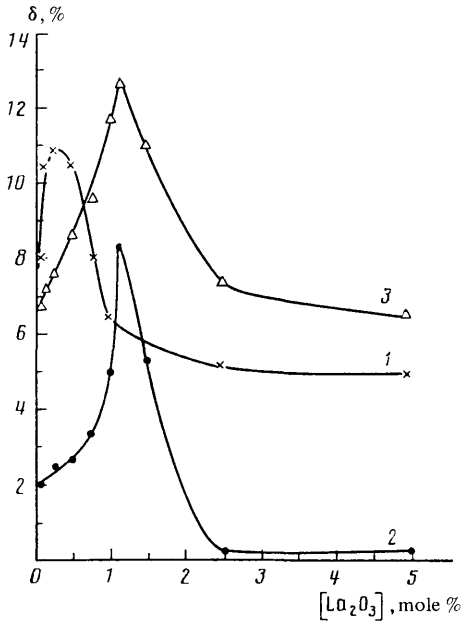


Figure 6. Dependence of the linear shrinkage (δ, %) of cerium dioxide on the concentration of added La_2O_3: *1*) first sintering (1673 K, 0.5 h); *2*) second sintering (1673 K, 2 h); *3*) third sintering (1773 K, 2 h).[10,45]

The results of experiments on the sintering of mixtures with the composition (80 – *x*) mole % CeO_2 + 20 mole % Nd_2O_3 + *x* mole % La_2O_3 in which *x* varied from 0 to 5 show that at the concentration indicated, the additives have an inhibiting action on the sintering of cerium oxide. A maximum was not observed, and the system showed only a regular poorly defined decrease in the rate of shrinkage, indicating that the effect of the reagents is additive. These experiments indicate that the added oxides M_2O_3 (from La to Yb, and also Y) react with the same defects of the CeO_2 matrix.

The properties of a modified cerium oxide ceramic have been studied.[39,47,48] In the range of additive concentrations 0.5 to 1.25 mole % La_2O_3, an extremal change in properties was observed. The processes of sintering, deformation, and crystal growth took place at maximum rates. The ceramic with the composition indicated had the optimum catalytic activity in the dehydrogenation of isopropyl alcohol.[49] With both decrease and increase in the additive concentration, the rate of sintering, deformation, and catalytic activity decreased, with corresponding changes in other properties.

Analysis of the results indicates a single mechanism of action of the microstructures on the processes being considered. The highest activity is observed when the thermodynamic state of the microstructure corresponds to the critical state where $a^0 = a_m$, $\Delta G_d = RT \ln(a^0/a_m) = 0$, where ΔG_d is the change in free energy on dissociation of the microstructure, a^0 and a_m the activity of the additive in the bulk of the crystal and in the microstructure respectively, R the gas constant, and T the temperature.

When the concentration of the impurity in the solid is lower than the equilibrium concentration and $a_m > a^0$, $\Delta G_d = RT \ln(a^0/a_m) < 0$, the microstructure is not formed, so that the additive does not have an activating effect.

The rate of deformation of the cerium ceramic is determined by the concentration of La_2O_3 in it. The efficiency of the influence of the microstructures formed by the impurities also depends on the temperature of the thermomechanical testing.[47,48]

With increase in the temperature of testing from 1473 K to 1573 K, the rate of deformation changes in different ways for specimens with different compositions. The fluidity increases considerably in the specimens containing 1.25 mole % La_2O_3, and is practically unchanged in the ceramic containing 5 mole % La_2O_3. With increase in temperature, the intensity of the relaxation processes evidently increases to the greatest extent in the thermodynamically unstable microstructures.

The increased thermal stability of the specimens containing 0.5 to 1.25 mole % La_2O_3 can be attributed to the high rate of the relaxation processes in the microstructures. According to phenomenological theory,[48,50] the stability of a material to thermal shock is due to the interaction of three forms of energy: the energy of elastic deformation, the surface energy, and the kinetic energy associated with the formation and growth of cracks. Expressions giving the relationship between the surface energy and the thermal stability of a material are given below. The Griffiths stress σ_g required to create cracks with dimensions c is related to the surface energy by the equation $\sigma_g^2 = 2\gamma E/\pi c$, where γ is the surface energy of the material, and E the modulus of normal elasticity.[48,50] The maximum temperature differential for which growth of cracks does not take place is given by

$$\Delta T = \left(\frac{2\gamma}{\pi c E}\right)^{1/2} \frac{1 + 2Nc^2}{\alpha}$$

where N is the number of cracks in the material on unit area, and α the coefficient of thermal expansion. In Ref.50 it is recommended that a material with a high surface energy be selected for articles subjected to thermal shock during use.

In the region of the critical state ($\Delta G_d = 0$), substances of different character show a heat capacity maximum;[51] as a result, the substances acquire an excess of energy by absorbing heat from the surrounding medium.

Under the conditions being considered, the surface structures in specimens of a CeO_2 ceramic containing 0.5 – 1.25 mole % La_2O_3 apparently have an excess of energy compared with the microstructures in specimens with either higher or lower La_2O_3 concentrations.

The catalytic action of the additives is due to the fact that the surface complexes in the critical state, formed as a result of the reaction of the substrate with the catalyst, have the highest reactivity and act as active centres in the transformation of the substrate.[39]

The microstructures forming restricted solid solutions on defects, and their influence on the thermomechanical properties of oxide ceramic materials, are examined below. In the $TiO_2 - Ta_2O_5$ system, XPES established[10] that in a surface layer with a thickness of 8 – 10 nm, tantalum is present as tantalum(V) in an octahedral environment of oxygen ions, as in Ta_2O_5.

Increase in the additive concentration is accompanied by an increase in the concentration of Ta_2O_5 in the surface layer, but its distribution coefficient decreases.[10]

[Ta_2O_5], mole %, in the bulk	0.001	0.1	3.0	5.0	10.0
[Ta_2O_5], mole %, in the surface layer	0.02	0.5	8.0	10.0	15.0
Distribution coefficient (K)	20	5	2.6	2	1.5

Experimental data[25] indicate that Ta_2O_5 dissolves in titanium oxide as the rutile-like compound $Ti^{III}TaO_4$. The possible formation of a solid solution in the $TiO_2 - Ti^{III}TaO_4$ system when titanium dioxide is added is due to the reduction of rutile in air at a temperature above 1370 K and the stabilisation of Ti^{III} when introduced into the solid solution.

At low concentrations (1 – 4 mole % Ta_2O_5), the additive had an inhibiting action on the sintering, and also lowered the fluidity and thermal stability of the ceramic at high temperatures. At a higher concentration of the additive, the rate of sintering, deformation, and thermal stability of the specimens increased. The dependence of the properties of the TiO_2 ceramic on the Ta_2O_5 concentration is given by curves with minima, correlating with the corresponding relationship for the free energy of the restricted solid solution.[46]

Similar relationships were established[16] in a study of the sintering of SnO_2 containing added Nb_2O_5. Increase in the concentration of added Nb_2O_5 from 0 to 0.05 mole % leads to suppression of the sintering; the shrinkage decreases from 11% to 6.3%. With further increase in the Nb_2O_5 concentration, intensification of the sintering is observed. Analysis of the X-ray electron spectra of specimens with the composition 99.8 mole % SnO_2 + 0.2 mole % Nb_2O_5 and 98 mole % SnO_2 + 2 mole % Nb_2O_5 showed enrichment of the surface layer in niobium by factors of 27 and 7 respectively. The energy parameters and valences of the Sn^{4+} and Nb^{5+} ions in the surface layer were the same as in SnO_2 and Nb_2O_5. In the surface layer of the tin(IV) oxide specimen, the added Nb_2O_5 forms restricted solid solutions, which are supersaturated at a concentration of 0.5 mole % or more Nb_2O_5. The solubility of Nb_2O_5 in SnO_2 is ~3 mass %.[52] Similar surface microformations were found in the $SnO_2 - ZnO$ system.[16] The surface phase consists of a solid solution with restricted solubility, with a higher concentration of the dissolved component, compared with the solid solution in the bulk.

Studies of various properties of an SnO_2 ceramic containing added ZnO showed that at concentrations of 0 – 0.5 mole % ZnO the shrinkage and thermal stability of the specimens remained unchanged, but the rate of sublimation decreased, corresponding to the existence of stable solid solutions in the surface layers. At ZnO concentrations greater than 0.5 mole %, its activating influence increased as a consequence of the decomposition of the surface solid solutions.

One promising method for preparing oxide materials with specified properties is by using modifying agents. Depending on their thermodynamic state, the microstructures formed by the impurities

may have either an activating or an inhibiting action on the physicochemical processes in the oxides in the synthesis and application of ceramic materials. If the impurity forms a chemical compound on the defects in the matrix, the formation of the micro-structure should take place via the stage of eutectic formation, depending on the concentration of the additive. Thermodynamic analysis[46] shows that the eutectic has the highest free energy, and the micro-formations in the eutectic state have the maximum reactivity. The critical state of the microstructure is reached at a definite concentration of the additive.

When the impurity forms solid solutions on the defects, activation is achieved in the critical state of the system, corresponding to supersaturation of the restricted solid solutions.

The established regularities of the formation of microstructures make it possible to use micro-additives to control the sintering and recrystallisation of dispersed solids, and also to produce specified properties such as the deformation, thermal stability, and ageing of ceramic materials at high temperatures.[9,10,16,39]

VI. SURFACE MICROSTRUCTURES AND THE PROTECTION OF CERAMIC MATERIALS FROM REDUCTION

One of the most important tasks in materials science is the production of ceramic condenser materials permitting high-temperature annealing in media with a low partial pressure of oxygen without loss of the dielectric properties. This task follows directly from the problem of replacing electrodes of valuable metals in ceramic condensers by electrodes of non-noble metals, whose annealing can be carried out only in a protective atmosphere with a low partial pressures of oxygen.

The processes taking place in the synthesis of materials permitting annealing in gaseous media with a low oxygen pressure have been described using the theory of point defects and the method of quasi-chemical reactions.[53–55] In the works cited, the equilibrium state of the point defects is assumed *a priori*, and the influence of impurities and additives on the properties of the material is regarded as a displacement of the equilibrium according to the law of mass action applied to the point defects. This model does not take account of physicochemical processes and the formation of surface microstructures.

XPES data[24,56] show that when additives which protect calcium titanate from reduction are introduced, the surface of $CaTiO_3$ granules has the composition $3CaO.TiO_2$, that is it differs from calcium metatitanate. The increase in the stability of the $CaTiO_3$ ceramic to reduction must be related to the formation of a surface structure which is enriched in CaO and which has an equilibrium oxygen pressure lower than that in the moist hydrogen used for annealing the ceramic. So long as reduction does not affect the surface phase, reduction of $CaTiO_3$ in the bulk does not take place, but the non-doped material may be reduced to a considerable extent under these conditions. The reduction begins at the surface, that is the defect zone, which moves into the depth during the process. The surface structure $3CaO.TiO_2$ formed increases the thermodynamic stability of the surface and the grain boundaries. Increase in the temperature of annealing and decrease in the partial pressure of oxygen in the furnace lead on prolonged treatment to reduction of the surface structure and the material in the bulk.

Similar results were obtained in a study of the protection of $SrTiO_3$ from reduction by adding SrO, BaO, MgO, and Ga_2O_3.[57] According to XPES data, in the specimens containing added Ga_2O_3, after heating in moist hydrogen, the surface layers of the ceramic did not contain gallium, because of the reduction of Ga_2O_3 to Ga_2O, which volatilised. Thus in the specimens in which titanium was replaced by gallium, the surface of the strontium titanate granules was enriched to the composition $\sim 7SrO.TiO_2$.

Examination of the reduction process from the viewpoint of surface phase formation makes it possible not only to obtain a consistent explanation of available experimental data but also to make specific technological recommendations for the production of materials which can be heated in media with a low partial pressure of oxygen.

VII. THE INFLUENCE OF SURFACE STRUCTURES ON THE ELECTRICAL PROPERTIES OF CERAMIC MATERIALS

Oxide materials with dielectric, semiconducting, or highly conducting properties with electronic or ionic carriers are synthesised by controlling the chemical character and concentration of impurities. The mechanism of the action of the impurities has been insufficiently studied, however.

The titanium-containing compounds TiO_2, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ and solid solutions based on them are widely used in electronics. The properties of TiO_2 containing Ta_2O_5 have been studied.[58] In Ref.59 it was suggested that the semiconducting properties of doped titanium dioxide are due to the production of titanium(III), but the reasons for its appearance were not established. Magnetochemical and XPES data [58] showed that Ta_2O_5 dissolves in titanium dioxide to give the rutile-like compound $Ti^{III}TaO_4$. The possible formation of a solid solution when titanium dioxide is doped is due to the reduction of rutile in air at a temperature above 1370 K and the stabilisation of Ti^{III} in the solid solution.[13] The formation of the $TiO_2-Ti^{III}TaO_4$ solid solution leads to a decrease in the specific electrical resistance of the specimens by factors of 10^8-10^{10} at concentrations of 0.1–5 mole % Ta_2O_5. When the limit of the solubility of Ta_2O_5 in TiO_2 at the grain boundaries is exceeded, decomposition and oxidation of the $TiO_2-Ti^{III}TaO_4$ solid solution takes place to give dielectric layers with the composition $TiO_2 + TiTa_2O_7$ on the surface of the granules. Thus the extremal concentration dependence of the conductivity of TiO_2 doped with Ta_2O_5 is due to two competing reactions: the formation and decomposition (oxidation) of the $TiO_2-Ti^{III}TaO_4$ solid solution.[57]

The influence of the combined additives Nb_2O_5 and BaO on the electrophysical properties of TiO_2 has been studied.[60] When the niobium(V) cations are added, the specific electrical resistance of the material decreased from 10^{13} Ω.cm to 100 Ω.cm at 300 K. Auger spectroscopy detected the segregation of barium along the grain boundaries of the titanium dioxide ceramic; the distribution coefficient of barium reached 150. The action of the added Nb_2O_5 was explained[60] using the disordering model:

$$Nb_2O_5 = 2Nb_{Ti}^{\cdot} + 2e^- + 4O_O + {}^1/_2O_2$$

where $Nb_{Ti}^{\cdot}$ is the cation occupying a cation site in the TiO_2 lattice; O_O an oxygen ion in a normal position (in a lattice site); and e^- an electron. This approach is inadequate, since it does not reveal the detailed mechanism of the physicochemical processes taking place in the reaction between the impurity and the matrix.

Niobium is an analogue of tantalum, and the formation and decomposition of the $TiO_2-Ti^{III}NbO_4$ solid solutions and the redox processes $Ti^{IV} \rightleftarrows Ti^{III}$ evidently determine the electrophysical properties of doped titanium dioxide. In Refs.58 and 61–64 it was shown

that the extremal dependence of the electrophysical properties of barium titanate when it is doped with the oxides of the lanthanides and the group V elements, so-called donor additives, is due to two competing processes in the barium titanate ceramic. On the one hand, semiconducting solid solutions containing titanium(III) [for example $Ba_{1-x}Y_x(Ti^{IV}_{1-x}Ti_x)O_3$] are formed, and on the other hand, oxidation and decomposition of the solid solutions take place (for example to give the compounds $BaTiO_3$ and $Y_2Ti_2O_7$), beginning on the surface and along the grain boundaries, as a result of which surface dielectric layers are produced. These physicochemical processes determine the extremal change in the properties of doped barium titanate: the magnetic susceptibility maxiimum, the dielectric–semiconductor transitions, and the existence of a positive temperature coefficient of electrical resistance close to the Curie point.

Materials whose properties are determined by the surface phases are used in electronics. These materials are used to prepare posistors (semiconducting ceramic devices having a positive temperature coefficient of electrical resistance), varistors (devices for which the dependence of the current on the voltage is appreciably non-linear), and condensers with an inter-granular capacity, in which a superhigh effective dielectric constant is produced since the capacities are included at the boundary of each granule. A ceramic for varistors based on zinc oxide has been studied repeatedly by electron microscopy. The segregation of Bi in a $ZnO-Bi_2O_3$ ceramic has been detected[65] at the boundary between the granules of the main material. The chemical form of the additive (MnO or MnO_2, CoO or Co_2O_3) has a significant influence on the distribution of the cations at the grain boundary and in the phase between the granules, and hence on the recrystallisation and microstructure of the specimen.[66] This is undoubtedly due to the formation of different surface structures when the oxides of metals in different oxidation states are added. Thus the monoxides MnO and CoO form solid solutions with ZnO, whereas when MnO_2 and Co_2O_3 are added, the spinels Zn_2MnO_4, $ZnMn^{III}_2O_4$, and $ZnCo_2O_4$ may be formed at the ZnO grain boundaries.

In an $SrTiO_3$ ceramic containing added Bi_2O_3, enrichment of the surface regions of the granules in Bi to a depth of up to 25 nm has been detected.[67] The influence of additives forming surface structures on the melting point of the layer at the grain boundaries, which plays a decisive role in crystallisation processes, has been noted.[68] It is suggested that selective fusion takes place, when the additives dissolve (fuse) the titanium dioxide which is always present in strontium titanate ceramic, with almost no change in the volume of the granule. An analysis of a large amount of experimental material led to the conclusion[69] that in a ceramic based on $SrTiO_3$ with added glass-forming oxides (Bi_2O_3, PbO, SiO_2): a) the second phase is concentrated in "pockets" at contacts between three granules; b) in general, the structure at the intergranular boundary is the same as that in the bulk, and the foreign ions merely enrich the outer layers of the granules; and c) the measured physical properties of the ceramic are determined by the oxidised layers of the granules on the semiconducting granule, and not by the second vitreous phase.

In the ferroelectric $BaTiO_3$, impurities (Bi, Zr) enrich the surface of the granules; the formation of a ferroelectric domain structure is suppressed in the granules, apparently as a result of the distortion of the $BaTiO_3$ lattice taking place on solution of the impurities.[70]

The development of methods for analysing a surface has made it possible to obtain direct experimental proof of the decisive role of surface structures in the production of various materials: ceramics for electronics,[71] electrode materials for fuel cells,[72] electrodes for the photolysis of water,[73] and semiconducting materials for devices with a Schottky diode.[74]

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Thus the study of the formation of surface microstructures and their influence on physicochemical processes in solids is an important research field. The nature of the influence of small quantities of impurity on the properties of a matrix is not completely clear, and contradictory explanations of the observed phenomena have been published. Theoretical studies are required in this field. The methods of physicochemical analysis used at present do not give exhaustive information on the properties of surface microstructures, so that it is necessary to improve further the methods for the quantitative analysis of the chemical composition, the determination

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The Paramagnetic Hydrophilic Probing of Colloidal Systems by NMR Spectroscopy

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The principal results of the use of a hydrophilic paramagnetic probe in ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy to study the structure, stability, and local density of packing of colloidal systems have been examined. The magnetic properties of the ions of *f*- and *d*-metals used as shift and relaxation probes have been discussed. Methods for estimating the stability of micelles and the conformation of the polar fragments of the molecules of surface active substances (SAS) on the surface of micelles and vesicles have been described. Particular attention has been paid to the study of dynamics, the compositional asymmetry of lipid membranes, the analysis of their interaction with physiologically active compounds, and the structure of biocolloidal systems.
The bibliography contains 134 references.

CONTENTS

I. Paramagnetic ions in NMR spectroscopy 717
II. The hydrophilic probing of micellar dispersions 718
III. The hydrophilic probing of liposomes 720
IV. The structure of biocolloidal systems 726

I. INTRODUCTION

NMR spectroscopy is one of the most effective methods for determining the structure of organic compounds and also supermolecular formations such as micelles, liposomes, and other complex colloidal aggregates. The informative character of NMR spectra, particularly proton NMR spectra, however, is lowered considerably because the nuclei of aliphatic groups not adjoining electronegative atoms give signals with similar chemical shifts. In addition, there are a number of factors leading to the broadening and the mutual overlap of the signals in the NMR spectra of colloidal systems. The most important of these are the presence of spin multiplets, dipole–dipole relaxation in the interaction of directly coupled nuclei, intermolecular association, the low fragmentary mobility of aliphatic chains, microheterogeneity, and the appreciable viscosity of dispersions.[1]

To overcome these difficulties and increase the informative character of the NMR spectra of colloidal systems, Soviet authors[2-9] proposed the method of hydrophilic shift and relaxation paramagnetic probes—the ions of *f*- and *d*-metals having an unpaired electron.

The influence of paramagnetism on the characteristics of nuclear resonance was detected by Bloembergen and Dickinson.[10] The characteristics of NMR in paramagnetic systems have been summarised in a number of reviews and monographs.[11-16] The interaction between the paramagnetic centre and the nucleus whose magnetic resonance is being observed is revealed in the isotropic hyperfine shift,[17] the change in the nuclear relaxation times T_1 and T_2,[18] and the nuclear polarisation of the spins as a consequence of the Overhauser effect.[19] These phenomena give information on the electronic and geometric structures of the ligands joined to the paramagnetic centres.

1. The Paramagnetic Shift

The isotropic shift of the signals in the NMR spectra of paramagnetic substances is the sum of two types of interaction: contact and pseudo-contact.

The Fermi contact shift takes place if the spin density of the unpaired electron is delocalised, and transferred to the nucleus through a system of chemical bonds. The contact shift obeys the Curie law, and for a one-spin state with an isotropic *g*-tensor it is described by the equation:[10]

$$\frac{\Delta H}{H_0} = -\frac{Ag\beta^2}{g_N\beta_N}\frac{s(s+1)}{3kT}$$

where A is the hyperfine interaction constant, g_N the nuclear *g*-factor, β_N the nuclear magneton, H_0 the intensity of the external magnetic field, β the Bohr magneton, g the Lande factor, k the Boltzmann constant, T the absolute temperature, and s the the spin-quantum number of the electron.

The contact shift of the signal is observed with the condition $T_{1e}^{-1} \gg A$, where T_{1e} is the electronic spin–lattice relaxation time. The contact shifts are large for the nuclei of oxygen and nitrogen directly coordinated to a paramagnetic centre, and also for carbon chemically bound to these atoms. For atoms at a greater distance and, commonly, for all protons, the contact contribution is small, and the observed paramagnetic shifts are pseudo-contact in character.[11-16]

The pseudo-contact shift of a signal is determined by the dipole–dipole interaction of the spins of the unpaired electron and the nucleus. It depends on the electron configuration of the paramagnetic ion, the magnetic anisotropy of the ligand field, and temperature. For axial symmetry of the complex, the pseudo-contact shift is given by the McConnell–Robertson equation:[17]

$$\frac{\Delta H}{H_0} = -\frac{\beta^2 s(s+1)}{9kT}(g_\parallel^2 - g_\perp^2)\frac{3\cos^2\theta - 1}{r^3} \qquad (1)$$

where $g_\parallel$ and $g_\perp$ are the components of the *g*-tensor of the magnetic anisotropy parallel to and perpendicular to the principal axis of the complex, r the distance from the paramagnetic centre to the nucleus, and θ the angle between the radius vector $\vec{r}$ and the principal axis of the complex.

The dependence of the pseudo-contact shift on the geometry of a complex, described by Eqn.(1), makes it possible to assign the signals in the spectrum of a ligand of known structure and to solve the inverse problem, that is from the known assignment to obtain information on the geometry of a molecule.[5,11-17]

2. Paramagnetic Broadening

In the presence of a paramagnetic centre, broadening of the NMR signals is observed, due to the increased rate of relaxation of the nuclear spin and the influence of exchange between the bonded and free molecules of the substrate. The spin–lattice T_1 and spin–spin T_2 relaxation times for nuclei with a spin of 1/2 in the presence of a paramagnetic centre are given by the Solomon–Bloembergen equations (2) and (3):[18]

$$\frac{1}{T_1}=\frac{2}{15}\frac{(\beta_N g_N \beta g)^2 s(s+1)}{r^6}\left(\frac{3\tau_c}{1+\omega_I^2\tau_c^2}+\frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right)+\frac{2}{3}s(s+1)\left(\frac{A}{\hbar}\right)^2\frac{\tau_e}{1+\omega_s^2\tau_e^2} \quad (2)$$

$$\frac{1}{T_2}=\frac{1}{15}\frac{(\beta_N g_N \beta g)^2 s(s+1)}{r^6}\left(4\tau_c+\frac{3\tau_c}{1+\omega_I^2\tau_c^2}+\frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right)+ + \frac{1}{3}s(s+1)\left(\frac{A}{\hbar}\right)^2\left(\frac{\tau_e}{1+\omega_s^2\tau_e^2}+\tau_e\right) \quad (3)$$

where ω_I and ω_s are the Larmor precession frequencies of the nucleus and the electron, and $\hbar = h/2\pi$ is Planck's constant.

The first terms of these equations are due to dipole–dipole interaction and depend on the distance r between the nucleus being observed and the paramagnetic centre. This interaction is determined by the correlation time of the electron–nucleus dipole interaction τ_c. The second terms, which are independent of r, are characterised by the correlation time of the contact interaction τ_e. The correlation times are defined as

$$\tau_c^{-1}=\tau_R^{-1}+\tau_s^{-1}+\tau_M^{-1}+\tau_D^{-1}$$
$$\tau_e^{-1}=\tau_s^{-1}+\tau_M^{-1}$$

where τ_R, τ_s, τ_M, and τ_D are the correlation times corresponding to the rotational motion, the relaxation of the electron spin, chemical exchange, and diffusion exchange respectively.

The relaxation times are influenced only by variable effects for which the correlation time has the same order of magnitude as the period of the Larmor precession of the nuclear spins.

II. THE HYDROPHILIC PROBING OF MICELLAR DISPERSIONS

The rapid decrease in the contribution of dipole–dipole interaction to the relaxation rates T_1^{-1} (2) and T_2^{-1} (3) with distance to the paramagnetic centre (r^{-6}) and the absence of its angular dependence make ions with high values of A and T_e (Mn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Gd^{3+}, etc.) valuable probes for structural studies. These ions are used as hydrophilic relaxation probes both to characterise the stability and local denisty of packing of micelles formed by different surface-active substances (SAS) and also to estimate the spatial orientation of the polar fragments in their structure.

1. Estimation of the Stability of Micelles

The stability of micellar aggregates is of fundamental interest both for solving the problems of micellar catalysis and in cell biochemistry. The estimation of the stability of micelles by the hydrophilic relaxation paramagnetic probe method[2–9] is based on the Dill–Flory statistical lattice model of the micelle.[20]

Paramagnetic cations can form dynamic complexes with the polar groups of SAS, oriented in micelles into the aqueous phase. The relaxation of the protons of definite fragments of the SAS molecule takes place only on the collision of the hydrated ion and the fragment of the molecule. It is therefore possible to determine whether the hydrophilic paramagnetic ions are in contact with definite parts of the molecule. An analysis[7,21–23] of the ^1H NMR spectra of micelles of sodium, copper, cobalt, and vanadyl dodecyl sulphate showed that not only the protons of the CH_2–SO_4^- groups but also the protons of the $(CH_2)_{10}$ chains and CH_3 groups collide effectively with Cu^{2+}, Co^{2+}, VO^{2+}, and lanthanide ions. These collisions may take place either as a result of the penetration of the ions into the micelles or as a result of the diffusional movement of the hydrocarbon chains into the Stern layer.[20,23,24]

The penetration of the hydrophilic ions into the hydrophobic nucleus of a micelle might be assumed in a model[25] containing water in the hydrophobic nucleus. The untenability of this model of "aqueous channels and cavities" within the micelle was proved, however, by the correspondence between the mechanisms of the extinction of the fluorescence of pyrene on ions in solution and in a micellar dispersion of sodium dodecyl sulphate in water,[26] and also by the difference between the experimental ratios of the spin–lattice relaxation times T_1 for the ^{13}C nuclei and the ratios calculated using the model of "aqueous cavities".[27] It has been proved convincingly[28,29] that in the micelle, only three or four methylene groups of the hydrocarbon chain of the SAS, counting from the polar head, are hydrated. Thus water is capable of penetrating into the hydrophobic nucleus of a micelle to a depth of only 0.4–0.5 nm. The positions at which water is localised in micro-emulsions (Tween-81–n-hexadecane–H_2O) have been determined by ^1H, ^2H, and ^{13}C NMR spectroscopy using Tb^{3+} and $Fe(CN)_6^{3-}$ ions as paramagnetic probes.[30] It was shown that the water molecules do not penetrate into the hydrophobic regions of the micro-emulsions. In addition, EPR spectroscopy detected hydrated Mn^{2+} ions only in the Stern layer of aqueous micelles of manganese dodecyl sulphate.[31]

These experimental data provide a reliable basis for estimating the stability of micelles using a relaxation probe.[32–36] The difference in the broadening of the signals from different molecular fragments of SAS in the presence of hydrophilic relaxation probes characterises the degree of stability of the micelle. The magnitude of the increase in the difference between the half-widths of the signals from groups close to the Stern layer (for example α-CH_2) and the terminal CH_3 groups of SAS molecules when paramagnetic ions (Mn^{2+}) are introduced into the dispersion of micelles.[32,34] This is confirmed by the experimentally established increase by two orders of magnitude in the difference in the relaxation rates ΔT_1^{-1} for the ^{13}C nuclei of the α-CH_2 and CH_3 groups of sodium dodecyl sulphate with increase in its concentration in water above the critical concentration for micelle formation (CCM) in the presence of Mn^{2+} ions.[27] The difference in the relaxation mechanisms is attributed to the increase in the constant for complex formation by Mn^{2+} ions with sodium dodecyl sulphate molecules on going from the solution to the micellar system.

Table 1 gives the values of the stability criterion for a number of micelles formed by the potassium salts of aliphatic acids.[34] Table 1 shows that the most stable micelles are formed by potassium stearate, and also by a mixture of synthetic aliphatic acids and sodium alkyl sulphonate, used in industry as emulsifiers in polymerisation.[32] The stability of the micelles decreases with decrease in the length of the hydrocarbon chain and increase in its unsaturated character. The influence of leuconol on the stability of micelles formed by the potassium salts of alkyl-substituted benzylbenzoic and aliphatic acids has been studied.[33,34] It was shown using Mn^{2+} ions that leuconol itself does not form micelles in water, and breaks down the micelles formed by other SAS.

On the other hand, if SAS molecules are capable of forming aggregates in the micelle structure, the stability of the micelles is increased. Aggregates of this kind with an average lifetime of ~10 ms and a stoichiometry which depends on temperature were detected in mixed micelles of sodium alkyl sulphonate and potassium dehydroabietate.[32] The influence of the stability of a layer of SAS adsorbed by the polymeric and monomeric particles on the micro-block character of emulsion copolymers was demonstrated in Refs.34, 37, and 38, and its influence on the rate constant of copolymerisation in Ref.33.

Table 1. Difference in the half-widths of the ^1H NMR signals of the α-CH_2 and CH_3 groups of SAS dispersions (0.1 M in D_2O)[34] and the values of the stability criterion.

SAS	$(\Delta\nu_{1/2}^{\alpha\text{-}CH_2}-\Delta\nu_{1/2}^{CH_3})$, Hz		Increase in $(\Delta\nu_{1/2}^{\alpha\text{-}CH_2}-\Delta\nu_{1/2}^{CH_3})$ when Mn^{2+} is added, Hz
	without Mn^{2+}	10^{-5} M Mn^{2+}	
Potassium stearate	0.70	2.70	2.00
Potassium palmitate	0.23	0.71	0.48
Potassium myristate	0.65	0.86	0.21
Potassium oleate	0.50	1.70	1.20
Potassium linoleate	0.08	0.40	0.32
Potassium linolenate	0.07	0.32	0.25
Mixture of synthetic aliphatic acids	0.83	2.57	1.74
Sodium alkyl sulphonate	3.1	4.4	1.3

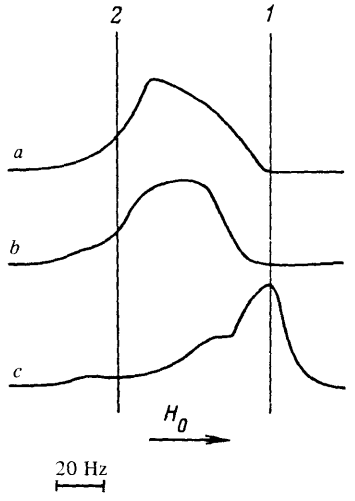


Figure 1. Form of the ^1H NMR signal of the oxyethyl protons in a 5% solution of Triton-X-100 in water in the presence of $TbCl_3$ (*a*), $Tb(NO_3)_3$ (*b*), and $Tb(ClO_4)_3$ (*c*); *1*) position of the signal of free polyhethylene glycol 1000 in the presence of these salts, *2*) position of the signal in the absence of the salts.[42]

An analysis of the characteristics of the bonding of paramagnetic ions to sodium dodecyl sulphate micelles in water[23,39] made it possible to put forward a method for measuring CCM from the cobalt-induced shift of the ^1H NMR signals of the SAS.[40] With increase in the concentration of the SAS above the CCM in the presence of Co^{2+} ions, a sharp increase in the chemical shift of the signals from the alkyl chains is observed, relative to the signal of acetone added to the system as standard. This phenomenon can be attributed to the sorption of the Co^{2+} ions in the Stern layer on micelle formation.

Similar studies carried out for non-ionogenic SAS[41] make it possible to probe their aqueous micelles.[42] For example, the observed anisotropy of the shift indeced by Tb^{3+} ions in the ^1H NMR spectra of Triton-X-100 and Triton-X-305 in water (Fig.1) was related to the existence of a salt concentration gradient along the thickness of the oxyethyl layer, depending on the counter-ion. These results agree with fluorescence measurements[43] and indicate that the penetrating power of electrolytes into micelles of non-ionogenic SAS is determined by electrostatic interactions at the micelle–water boundary.

VO^{2+}, Cu^{2+}, and Co^{2+} ions have been used[21,22,44] to study the micellar catalysis of the exchange of water protons in the coordination sphere of cations. This micellar catalysis has been related to the existence of an electrostatic potential on the surface of a sodium dodecyl sulphate micelle.[21] Micro-emulsification of this system with toluene leads to an increase in the rate of exchange.[22,44]

As paramagnetic centres for the analysis of colloidal systems it is possible to use iminoxyl markers, as has been done for micelles of ionic SAS containing phenoxy-groups.[45] Finally, it is possible to carry out the NMR probing of micelles by making use of the shifts induced by magnetically anisotropic (usually aromatic) substances and solvents.[46,47] The efficiency of these methods, however, is much lower than that of the hydrophilic paramagnetic probe, and the methods have not been developed.

2. Determination of the Conformation of SAS Molecules in the Structure of Colloidal Systems

Since the rates of relaxation of the nuclei and the induced shift of their signals in the NMR spectra depend on the distance r to the paramagnetic centre [Eqns.(1)–(3)], it is possible to estimate the preferred conformation and spatial orientation of the polar fragment of an SAS molecule in the structure of a colloid.[5,35,36,48,49] For small SAS molecules it is also possible to determine the conformation of the alkyl chains.[50,51] The conformation of the polar fragment generally remains unchanged on going from the SAS monomers in water to the micelles.[35,49] Thus the introduction of Mn^{2+}, Pr^{3+}, or Eu^{3+} into a dispersion of N-carbalkoxymethylene-2-methyl-5-vinylpyridinium bromides when their concentrations in water were above and below the critical concentration of micelle formation (CCM_1) showed that the conformation of the SAS molecule relative to the CH_2–COO bond remains eclipsed. However, on going from spherical to asymmetric micelles above CCM_2, the torsional angle increases, the conformation is no longer eclipsed, and the pyridine ring moves out of the plane of the monolayer.[35]

Similar changes in conformation in polymorphic transformations were detected in aqueous dispersions of mono-, di-, and triallylammonium salts with the general formula $(CH_2=CH\text{–}CH_2)_nN(CH_3)_{3-n}\cdot CH_2COORBr^-$, where n = 1–3, and monomers basxed on methacryloyloxyethylammonium salts $CH_2=C(CH_3)COOC_2H_4\overset{+}{N}(CH_3)_2\cdot CH_2COORBr^-$, where R = $C_{10}H_{21}$–$C_{16}H_{33}$.[36]

The magnitude of the selective broadening of the signals in the ^1H NMR spectra of anisotropic micelles, and an analysis of the structure of SAS molecules using models, made it possible to use Eqn.(3) to estimate the preferential conformation of the polar fragment (Fig.2). The areas corresponding to the molecule, calculated for these conformations, show good agreement with those determined experimentally

at a water–air interface.[36] The stabilisation of the monolayer on going from asymmetric micelles to a lamellar structure is accompanied by the movement of the methacrylate and N-methyl groups into the aqueous phase.[36,48] This is indicated by the increased broadening of the signals from the corresponding fragments when Mn^{2+} ions are introduced (Table 2). The conclusions reached about the relationship between the conformation and spatial orientation of the polar fragments of surface-active monomers and their polymorphism in water made it possible to understand the regular features of their emulsion polymerisation.[35,36,48,52]

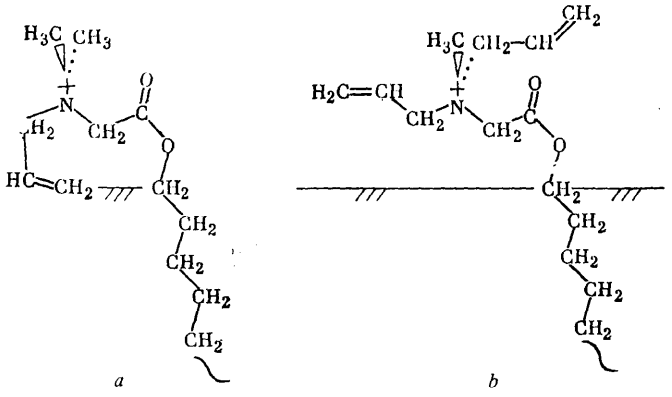


Figure 2. The conformation of alkylammonium SAS in asymmetric micelles: *a*) $n = 1.3$; *b*) $n = 2$.[36]

Table 2. Values of the broadening induced by Mn^{2+} cations for the ^1H NMR signals of dispersions of N-cetyl-N,N-dimethylmethacryloyloxyethylammonium bromide in water.[36]

Proton group	$\Delta\Delta\nu_{1/2}$, Hz*	
	asymmetric micelles	lamellae
CH_3 (terminal)	0.01	0.02
$(CH_2)_n$	4.28	0.60
CCH_3	1.04	1.50
$\overset{+}{N}CH_3$	1.50	2.45
α-CH_2	8.06	broadened
=CH(trans)	5.18	broadened
=CH(cis)	5.18	broadened

*$\Delta\Delta\nu_{1/2} = \Delta\nu_{1/2}([Mn^{2+}] \neq 0) - \Delta\nu_{1/2}([Mn^{2+}] = 0)$.

An analysis of the conformations of the alkyl fragments of sodium dibutyl phosphate in solution and in a micelle using Ni^{2+} and VO^{2+} ions[50] made it possible to select the most probable conformations of the POCCCC chain. Table 3 shows that the probability of a number of conformers increases on going from the SAS solution to the micelles. The use of Mn^{2+} ions as paramagnetic probes showed that the alkyl fragments of the SAS do not enter the aqueous phase. The first segment of the chain has an almost *trans* conformation, although the conformation of the subsequent segment is the same as in the liquid hydrocarbon.[51]

Thus polymorphic transformations in colloidal systems produce a change in the conformation of not only the hydrophilic but also the hydrophobic fragments of the SAS molecule.

Table 3. Probabilities of the alkyl chain conformers of sodium dibutyl phosphate.[50]

Conformer	P	
	monomer	micelle
TTT	0.132	0.200
$TTG^+ + TTG^-$	0.067	0.086
$TG^+T + TG^-T$	0.057	0.086
$G^+TT + G^-TT$	0.057	0.062
$TG^+G^+ + TG^-G^-$	0.029	0.037

Note: *P* is the probability of the conformer, *T* is the *trans*-rotamer, and *G* the *gauche* rotamer.

III. THE HYDROPHILIC PROBING OF LIPOSOMES

The method of hydrophilic paramagnetic probing opens up extensive possibilities for the study of the structure and molecular dynamics of lipid membranes, which are closed lamellae. It makes possible the differential observation of the signals from molecules situated on the external and internal surfaces of a bilayer vesicle.[2–6,8,9] From the ratio of the integral intensities of these signals it is possible to estimate the size of the membrane particles, and also to detect asymmetry of the molecular composition, that is differences in the distribution of lipids, proteins, and other components between the external and internal surfaces of a membrane. The method makes it possible to estimate the conformation and spatial orientation of the polar fragments of lipid molecules facing the aqueous phase. It makes it possible to study the processes of trans- and inter-membrane transfer of ions, lipid molecules, proteins, and all possible biologically active compounds.

Various aspects of the application of the hydrophilic paramagnetic probing of vesicles and biological membranes have been reviewed.[9,53–58]

1. The Differentiation of the Surfaces of Membranes by NMR Spectroscopy and the Estimation of the Dimensions of Liposomes

The testing of the bilayer character of liposomes of amphoteric lipids in water can be carried out using paramagnetic lanthanide ions.[3–5,8,9,59–73] and for anionic lipids using divalent manganese ions[2,3,6,9,74–82] or inorganic anions[46,80–83] which do not bring about flocculation of the colloidal system.

When shifting ions are introduced into the external volume of a dispersion of phosphatidylcholine (PC) in water, subjected to ultrasonic treatment, the ^1H NMR spectrum (Fig.3c) shows two signals from the protons of the polar group. The chemical shift of one of these signals coincides with that of the signal from the "pure" dispersion (Fig.3*a*), and corresponds to polar groups facing into the vesicle. The other is due to external polar groups coordinated to the lanthanide ions.[3,9,59,60] The directions of the shift of the signals are of opposite sign, and the broadening effect of the ion is determined by the absolute magnitude of the anisotropy factor of the magnetic susceptibility.[9,60]

A similar differentiation of the internal and external surfaces of a vesicle can be carried out from the ^{13}C [8] (Fig.4) and ^{31}P [4] (Fig.5) spectra. The observed ratios of the integral intensities of the external and internal signals from the polar groups (I_{ext}/I_{int}) are 2.09 for PC and 2.03 for sphingomyelin (SM) in water. [9]

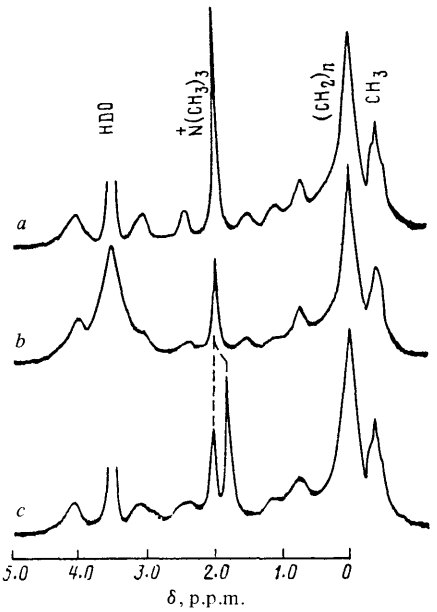


Figure 3. ^{1}H NMR spectra of a 5% dispersion of egg PC subjected to ultrasonic treatment: *a*) in D_2O; *b*) after the addition of 10^{-3} M $MnSO_4$ or *c*) 10^{-2} M $Eu(NO_3)_3$ to the external volume of the specimen.[3]

Nd^{3+} and Eu^{3+} ions have been used[61-63] to test the bilayer character of liposomes of synthetic saturated PC (C_{10}–C_{16}) and phospholipids containing polymerised itaconic acid fragments. Increase in the length of the alkyl chains in the PC molecules leads to the formation of more stable vesicles.[61] The addition of dipalmitoyl-lecithin, bis(2,4-octadienoyl)-PC, or cholesterol to unstable vesicles of itaconate-containing phospholipids gives two kinds of stable bilayer liposomes with diameters of 40 nm and 140 nm.[62,63]

By placing in the vesicles and in the external medium different paramagnetic probes (for example Pr^{3+} and Eu^{3+}) which shift the signals from the polar groups to weak and strong fields respectively, it is possible to make the method highly sensitive and at the same time to follow processes taking place on the external and internal surfaces of the bilayer.[64,65]

The influence of paramagnetic probes on the thermal phase transformations in aqueous dispersions of lipids has been studied.[59,67-70] For example, for dipalmitoyl-lecithin the introduction of Pr^{3+} ions raises the phase transition point by 3–5 K.[59,67]

The systematic error of the determination of the ratio I_{ext}/I_{int} at ^{31}P nuclei,[73] produced as a result of the decrease in the nuclear Overhauser effect (NOE) on the signal from the nuclei in contact with the paramagnetic probe, with decoupling from the protons does not exceed 10% for PC.[9] To obtain a more accurate result, it has been suggested that the dispersion be titrated with a relaxation probe (Mn^{2+}, Ni^{2+}, Gd^{3+}) by recording the ^{1}H [2,3,74,75] or ^{31}P [74-77] NMR spectra. It should be noted that the measurement of the ratio of the intensities in Ref.74 was incorrect; instead of the peak intensities, the integral intensities should have been measured.[76]

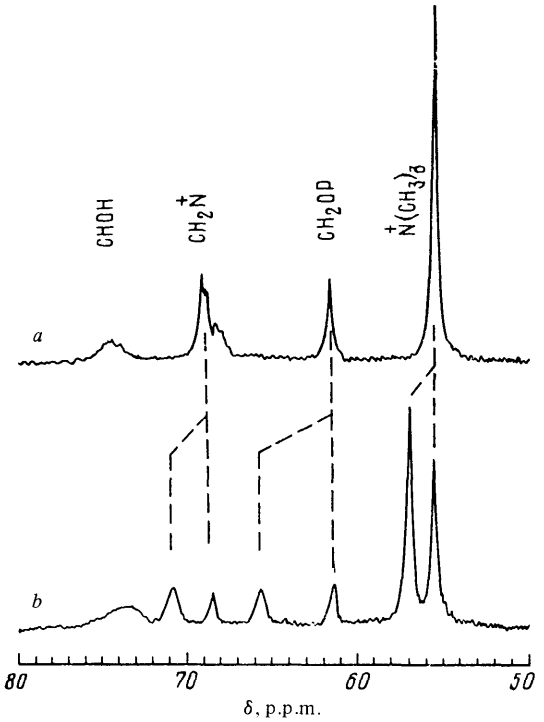


Figure 4. Range of the choline signals of the ^{13}C {H} NMR spectrum of a 20% SM dispersion subjected to ultrasonic treatment: *a*) in D_2O; *b*) after the addition of 5 x 10^{-2} M $Pr(NO_3)_3$ to the external volume of the specimen.[8]

Fig.6 shows that the dependence of the intensity of the ^{31}P signal on the concentration of Mn^{2+} in the external volume comes to a plateau corresponding to the intensity of the signal from the internal phosphate groups.[76,77] For phosphatidylinositol (PI), I_{ext}/I_{int} is 2.50.

Since according to X-ray diffraction data the thickness of the bilayer is 3.6 nm,[78] the external diameters are 24 nm for vesicles of PC and SM, and 19 nm (±1 nm) for vesicles of PI.[9] The values obtained agree with the results obtained by other methods.[79]

The titration of a system containing bilayer vesicles of PC gives two ^{1}H NMR signals from $\overset{+}{N}(CH_3)_3$ groups (the spectra were recorded at 250 MHz).[80] The signal from the internal $\overset{+}{N}(CH_3)_3$ groups is displaced by 0.01–0.02 p.p.m. towards higher fields. The magnitude of the shift increases with the time of ultrasonic treatment of the dispersion. Measurement of the relaxation times T_1 of the ^{13}C nuclei of the external and internal $\overset{+}{N}(^{13}CH_3)_3$ groups of enriched PC[71] showed that this shift is due to a difference in the packing and mobility of the molecules on the external and internal surfaces of the bilayer. This was previously noted in a study[81] using Mn^{2+} ions,

and not Yb^{3+} ions, as in Ref.71. Two-component ^{13}CO [8] and ^{31}P [77,82] signals were also obtained in the spectra of phospholipid vesicles. The observed influence of the density of packing of the molecules on the magnitude of the chemical shift[80,81] made it possible to discriminate the NMR signals (500 MHz) from monomers, micelles, and vesicles of PC, phosphatidylaminoethanol (PA), and SM using Pr^{3+} cations.[72] In these systems the vesicles were obtained without ultrasonic treatment by adding short-chain phospholipids.

A method has been proposed[34] for estimating the average dimensions and number of bilayers n in multilayer liposomes. The integral intensity of the signal from the polar groups, remaining in the titration with Mn^{2+} ions, makes it possible to determine the ratio I_{ext}/I_{int}. This ratio depends on n and R/d, where R is the external radius of the liposome, and d the thickness of the bilayer. It was shown that the ratio of the lengths of the alkyl chains in lipid-like SAS determines the structure of the liposome. Thus for liposomes of N-cetyl-N,N-diallyldodecylacetoammonium bromide with an average diameter of 1000 nm, $n = 13 \pm 1$, whereas liposomes of N-dodecyl-N,N-diallylcetylacetoammonium bromide with an average diameter of 25 nm are bilayer.

2. Factors Influencing the Lifetime of the Hydrophilic Probe in the Bound State

The lifetime of the paramagnetic probe in the state combined with the membrane determines the magnitude of the induced shift of the signals in the NMR spectra. The point of binding of the paramagnetic ions is the phosphate group of the phospholipid molecule.[4,5,8] The maximum number of Mn^{2+} ion binding positions on the surface of a PC membrane is 0.005 per PC molecule,[85] and the corresponding number for the lanthanides (Pr^{3+}, Nd^{3+}) is 0.13.[59] The presence of a single shifted signal in the NMR spectra when the lanthanides are introduced into a phospholipid dispersion indicates a high rate of lateral exchange of the ions between the binding position. The lifetime of the ions in the bound state is independent of their concentration in solution, but decreases with increase in the PC concentration from 0.17 s (at 0.06 M PC) to 0.02 s (at 0.18 M PC).[9] The lifetime of the probe in the bound state is a maximum at pD = 3.5 and decreases on heating.[9]

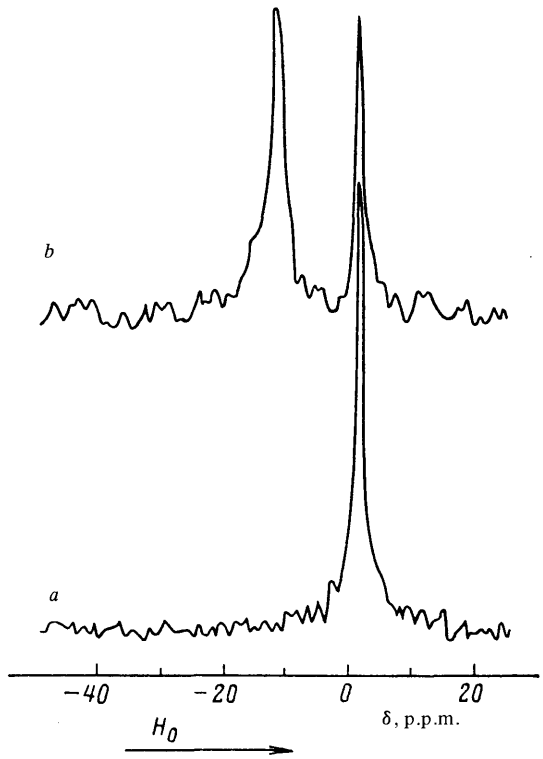


Figure 5. ^{31}P $\{^1H\}$ NMR spectra of a 10% dispersion of egg PC subjected to ultrasonic treatment: *a*) in D_2O; *b*) after the addition of 10^{-2} M $Pr(NO_3)_3$ to the external volume of the specimen.[4]

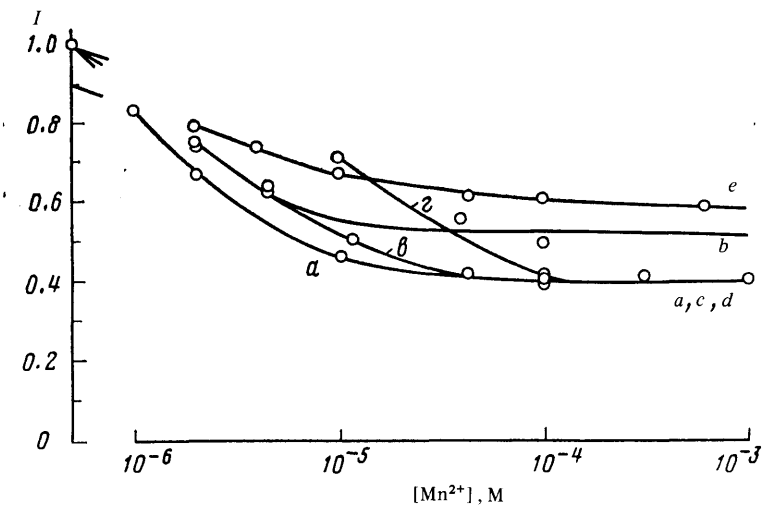


Figure 6. Dependence of the integral intensity (I) of the ^{31}P NMR signal on the Mn^{2+} concentration for dispersions of 0.08 M PI (*a*);[73] 0.05 M (PC + PG) mixture, 1:1, mole/mole, *b*) PC, *c*) PG; and the corresponding dependence for the $\overset{+}{N}(CH_3)_3$ ^1H NMR signal for dispersions of 0.05 M PC (d) and a (PC + PG) 1:1 mole/mole mixture (*e*)[71] in D_2O.

The inclusion of anionic lipids (PI and phosphatidytlserine PS) in the lipid bilayer leads to an increase in the paramagnetic shifts of the signals from the polar groups.[8,76,77] These lipids, by giving the surface of the bilayer a negative charge, influence the distribution of ions in the Stern layer of the vesicle. As a result, the lifetime of the probe in the bound state increases.[9] The same phenomenon is responsible for the influence of inorganic anions on the magnitude of induced shifts.[4,8,46,53,86,87] In this case, however, the redistribution of the ions takes place as a result of the selective Langmuir adsorption of anions on the surface of the lipid bilayer.[87] The ratio of the anion binding constants K correlates satisfactorily with the ratio of the electrophoretic mobilities of liposomes in the presence of these anions (Table 4).[86,87]

Table 4. Electrophoretic mobility of PC liposomes in solutions of different potassium salts and the constants of the Langmuir adsorption isotherms for different anions (300 K, pD = 6).[87]

Anion	Mobility, $\mu m\ s^{-1}\ V^{-1}\ cm$	Δ, p.p.m.	K, $mole^{-1}$
Cl^-	−0.15±0.01	0 15±0.01	1.67±0.45
NO_3^-	−0.46±0.03	1.01±0.02	4.03±0.26
SCN^-	−1.85±0.11	0.99±0.01	23.7±1.1
SO_4^{2-}	1.25±0.09	−0.43±0.01	14.9±0.2

3. Determination of the Conformation and Spatial Orientation of Polar Fragments

The dipole–dipole broadening of the signals in the NMR spectra of colloidal systems prevents the direct use of spin–spin coupling constants to estimate the conformation of polar groups. Thus in Refs.5, 8, and 49 the conformation and spatial orientation of phosphorylcholine zwitterions on the surface of vesicles were determined using the relative pseudo-contact shifts induced by Eu^{3+}, Pr^{3+}, and Yb^{3+} for the signals in the ^1H and ^{13}C NMR spectra. The experimental values of the shifts together with the values calculated from Eqn.(1) for all possible 54 P–O, O–C, and C–C bond rotamers (Fig.7) were plotted on maps of the relative induced shifts of the ^{13}C and ^1H nuclei (Fig.8).

The main contribution to the conformation of the zwitterion is made by the *trans*-forms 111, 211, 611 (70–83%),[5,49] and their probability increases with the degree of unsaturated character of the hydrocarbon chains and with increase in temperature. This is apparently related to the increase in the area corresponding to the SAS molecule[28] and agrees with D and ^{31}P NMR data.[88]

The conclusions obtained are confirmed for O–C bond rotamers by an analysis of the vicinal spin–spin coupling constants $^3J_{POOCC}$ [49] and $^3J_{POCH}$,[89] found without the introduction of a paramagnetic probe. Thus paramagnetic ions have no significant influence on the conformation of a polar group on the surface of a vesicle, so that the fears expressed on this account in Refs.15 and 90 are unfounded.

In micelles of lysolecithin and glycerophosphorylcholine diacetate, instead of the *gauche* forms 132 ≡ 123 and 323 ≡ 532, the different set 523 ≡ 332 is produced,[49] in agreement with the results of studies[91,92] in which a paramagnetic probe was not used.

The fact that the NMR signals from the phosphorylcholine nuclei and from the CH_2CH_2CO groups of the aliphatic acid chains have induced shifts with different directions indicates, in accordance with Eqn.(1), that for all selected conformations the phosphorylcholine zwitterion is arranged parallel to the membrane surface.[5,8,49] This conclusion was subsequently confirmed by other methods: measurement of the ^{31}P NOE in vesicles,[93,94] the ^{31}P NMR of oriented bilayers,[95,96] neutron diffraction (for PC),[97] X-ray diffraction (for PA),[98] measurement of the anisotropy of the ^{31}P shift and D NMR for both PA[99] and PC,[100,101] and quantum-chemical calculations.[102] Thus paramagnetic ions do not alter the orientation of a polar group at the phase interface.[5,9,49,103]

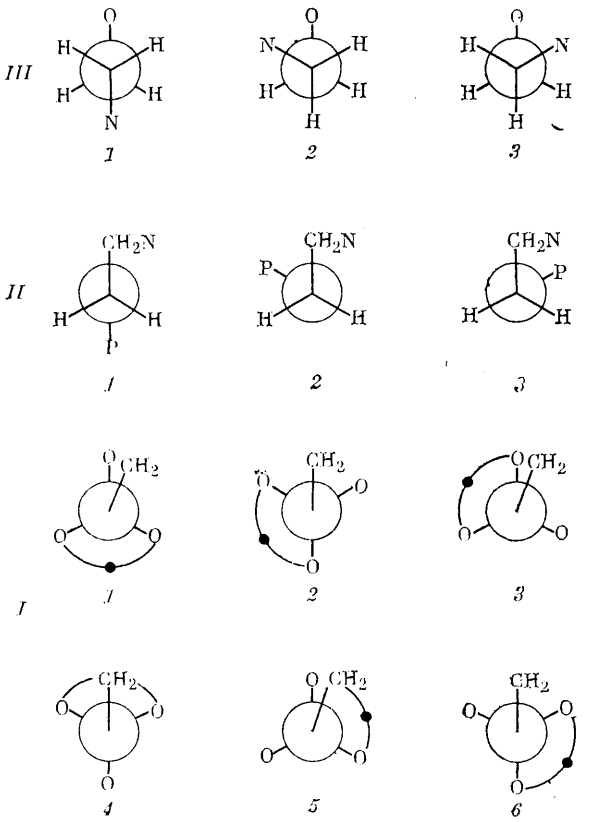


Figure 7. Rotamers of the phosphorylcholine group with respect to the bonds P–O (I), O–C (*II*), and C–C (*III*).[49].

From this it follows that it is not correct to transfer the conclusion about the normal arrangement of the zwitterion on vesicles, obtained for planar bilayers.[104,105] It was noted above that on going from non-closed lamellar structures to bilayer liposomes, the spatial orientation of the polar fragment changes from normal to the surface of the bilayer to planar.[36]

The main reason for the stabilisation of the unfolded *trans*-conformation and the planar orientation of the phosphorylcholine zwitterion on the surface of the vesicle is apparently the intermolecular interaction between the phosphate and $\overset{+}{N}(CH_3)_3$ groups of neighbouring molecules.[49,102] This conclusion is of fundamental importance for an understanding of the molecular organisation and functioning of biological membranes.

4. The Exchange of Lipid Molecules and the Compositional Asymmetry of Membranes

Liposomes, like micelles, are dynamically stable structures. The molecules of SAS in liposomes are extremely mobile, however. They take part in three types of transfer: lateral diffusion,[106] trans-membrane transfer,[107] and inter-membrane transfer.[76] The ratio of the rates of these processes depends on the structure of the lipid molecules and the colloidal system, the molecular composition of the bilayer, and external factors (temperature, ionic strength, the presence of transport proteins, etc.). This ratio determines the possible formation of liposomes with an asymmetric composition of the external and internal monolayers, and also of molecular clusters in the monolayer.

The hydrophilic paramagnetic probe method is the most effective both for the study of the three types of molecular exchange[5,65,76,77,108-110] and in the analysis of the molecular topography of colloidal systems.[64,65,73-77, 111-114]

The rate of the trans-membrane transfer of lipid molecules is low. The time constant of the process is greater than 2.2×10^4 s for egg PC[107] (determined by the spin probe method) and 4.3×10^4 s for [N−$^{13}CH_3$] dioleoyl PC[108] (determined from the penetration of Pr^{3+} ions through the bilayer) at 350 K. This rate can be increased, however, by modelling the bilayer by a system of inverse micelles[5,109] or by introducing small quantities of lysolecithin (LPC) and peroxides.[65,110]

In Refs.5 and 109, the rates and thermodynamic parameters of exchange were found using a mixture of inverse micelles of PC in benzene, with and without Mn^{2+} or Pr^{3+} ions in the solubilised aqueous vesicle.

The kinetics of the trans-membrane transfer of molecules of PC[110] and PI[65] in the presence of LPC or peroxides has been studied by introducing Pr^{3+} or Yb^{3+} ions on the outside of the vesicles. The use of a double probe technique[64] showed that in the transfer of PI molecules the decrease in the induced shift of the signal from the external $\overset{+}{N}(CH_3)_3$ groups is accompanied by an increase in the shift of the signal from the internal groups. The results obtained for both inverse micelles and vesicles indicate that the trans-membrane transfer of the molecules is cooperative in character.

Inter-membrane exchange by lipid molecules is initiated either by a transport lipid-binding protein or by LPC.[76,77] The analysis of the kinetics of the process was based on the increase in the induced paramagnetic shift of the signals from the polar groups when molecules of

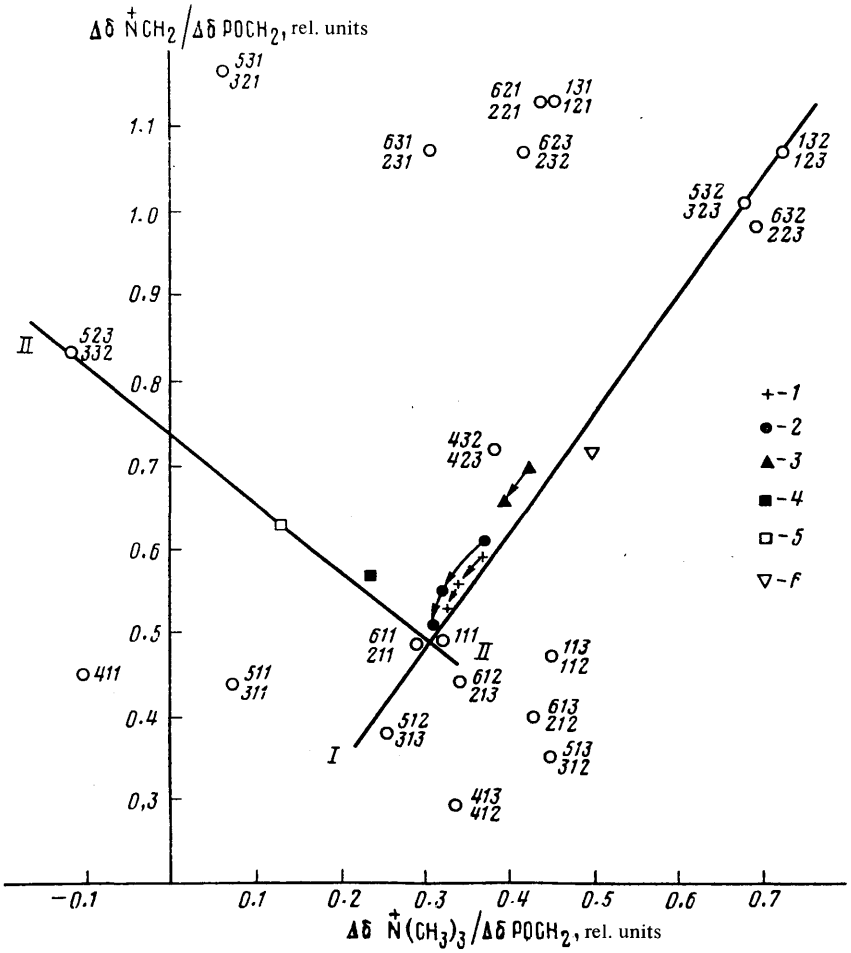


Figure 8. Map of the induced shifts for the ^1H nuclei of the zwitterion: *1*) egg PC, *2*) dioleoyl-PC, *3*) dipalmitoyl-PC, *4*) lysolecithin, *5*) glycerophosphorylcholine diacetate, *6*) stearylphosphocholine.[49]

an anionic lipid (PI) were built into the bilayer (Figs.9 and 10). The change in the magnitude of the induced shift and the ratios I_{ext}/I_{int} give information on the mechanism of inter-membrane exchange.

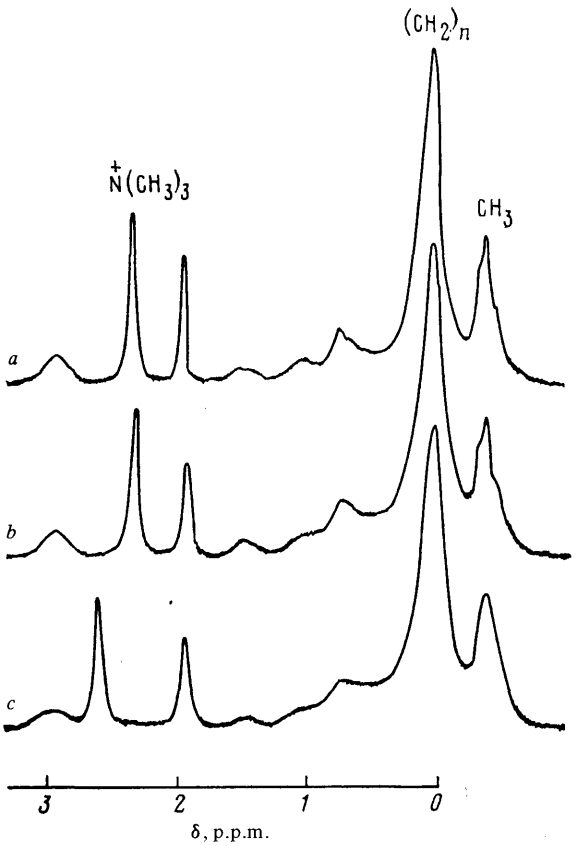


Figure 9. ^{1}H NMR spectra of phospholipid dispersions in D_2O after the addition of 10^{-2} M Pr^{3+} to the outside: *a*) PC vesicles, *b*) mixed vesicles of PC and PI before and *c*) after the exchange of PI by the action of a transport protein (323 K).[77]

In the exchange, vesicles with an asymmetric distribution of lipids are formed (Fig.11). In the spontaneous exchange of PC and PI molecules[65] or in the presence of a PI-transporting protein, PI is exclusively built into the external monolayer.[77] If the system contains micelles of LPC, PI is localised chiefly in the internal monolayer. Monomolecular exchange takes place in the first case, and cooperative exchange in the second. The $^{13}C[N-{}^{13}CH_3]$ NMR spectra of palmitoyl LPC, built into vesicles of dioleoyl-PC, in the presence of Dy^{3+} showed that LPC itself is localised in the external monolayer of the vesicle.[111]

The curvature of the bilayer also leads to an asymmetric distribution of lipids. In mixed PC–PG vesicles, the phosphatidylglycerol (PG) molecules are present chiefly on the external surface,[74,75] as shown by ^{31}P and ^1H NMR with Mn^{2+} This distribution is difficult to understand, since other anionic lipids of PS[64,82] and PI[61] are situated chiefly in the internal monolayer, as indicated by more accurate data with two probes, Pr^{3+} and Eu^{3+} (Fig.10). This distribution is attributed to the more compact packing of the molecules in the internal monolayer, as a result of which the bulky polar fragments of PC are more effectively arranged in the external monolayer. With increase in the concentration of PC or PI, however, the electrostatic forces of repulsion displace an increasing number of molecules of the anionic lipids into the external layer, and the asymmetry of the membrane decreases.[64,65]

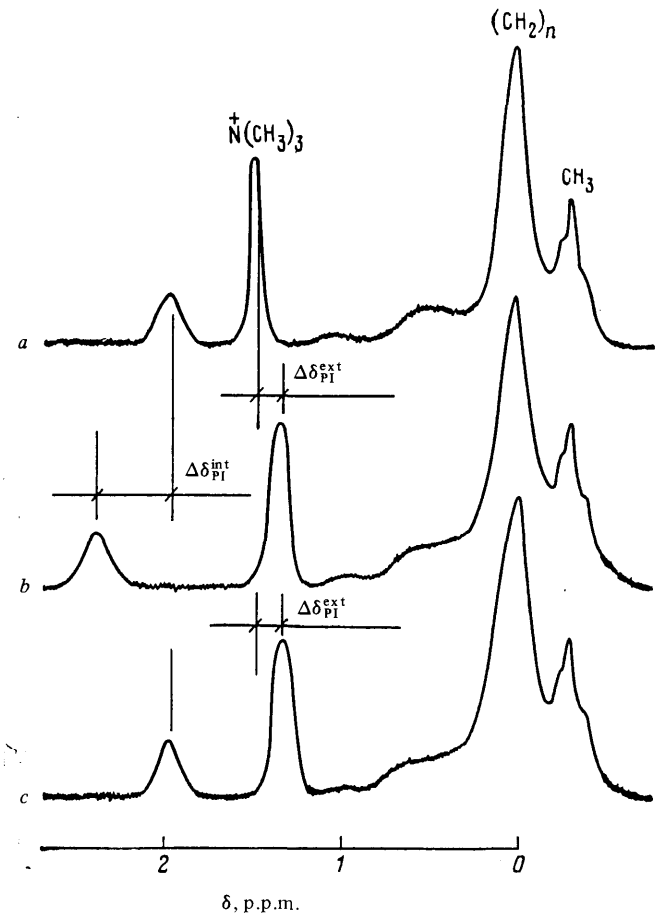


Figure 10. ^{1}H NMR spectra of phospholipid dispersions in D_2O: *a*) PC vesicles, *b*) mixed vesicles of PC and PI, subjected to ultrasonic treatment, *c*) vesicles of PC with spontaneously built-in PI after the combined incubation of vesicles of PC and PI for 5.8 x 10^4 s at 296 K, containing 10^{-2} M Pr^{3+} inside and 10^{-2} M Eu^{3+} outside.[65]

The asymmetry of the distribution of cholesterol in vesicles of PC was also first detected using a paramagnetic probe (Pr^{3+}).[112] Cholesterol is present in the external monolayer in vesicles of unsaturated PC, and is distributed throughout the vesicles of saturated PC.[113] The constant for the spontaneous inter-membrane exchange of cholesterol is 0.0117 min^{-1}.[113]

The rate of the lateral diffusion of cholesterol depends on the molecular structure of the PC.[53,114] Thus if the liposomes contain simultaneously molecules of the SS-, SU-, and UU-types (S and U represent respectively saturated and unsaturated alkyl chains), the cholesterol is more frequently in contact with molecules of the UU-type than with molecules of the SU- or SS-type. Thus if the membrane contains PC of different types, the cholesterol is present chiefly in the phase containing the more unsaturated molecular forms of PC.

5. Analysis of the Interaction of Liposomes with Low-Molecular-Weight and Biologically Active Compounds

The above example of the study of the behaviour of cholesterol molecules in the structure of liposomes indicates the promising possibilities provided by the use of the paramagnetic probe method to investigate the nature of the interaction of physiologically active compounds with a membrane. Most studies are based on the use of the effect on the trans-membrane transfer of lanthanide cations of ionophors,[66,115-117] local anaesthetics,[118,119] and other physiologically active compounds,[76,77,120] as in the case of LPC.[110]

The transport of Pr^{3+}, Eu^{3+}, Yb^{3+}, and Dy cations through a bilayer has been studied using the ionophor X-537A,[115] alamethicin,[116] the ionophor A23187 of the nigericin type,[117] glycophorin,[66] the local anaesthetics tetracaine, procaine, and lidocaine,[118] isoprenoids,[119] and sodium taurocholate.[120] Here, the lanthanide cations act as physiological analogues of calcium. The activation energy of the process is 85 kJ $mole^{-1}$.[119]

A different method has been proposed for determining the kinetics of the transport of Na^+ and Li^+ by the ionophor monensin using Gd^{3+} as relaxation probe. Since the order of magnitude of the rate of transfer was the same as that of the rate of relaxation of the ^{23}Na and ^7Li nuclei, the mobility of the ions made a contribution to the relaxation time. The values found, $\nu_{Na} = 4$ nm s^{-1} and $\nu_{Li} = 0.035$ nm s^{-1} correspond to the affinity of the ionophor for cations.[121]

^{13}C-enriched lipids have been used for the paramagnetic hydrophilic probing of the distribution of aliphatic acids in vesicles of PC with a pH gradient.[58] The relaxation probe Mn^{2+} established that the 1-anilinonaphthalene-8-sulphonate molecule is localised on the surface of the vesicles.[122]

IV. THE STRUCTURE OF BIOCOLLOIDAL SYSTEMS

The transport of ions through a membrane barrier plays a fundamental role in the vital activity of cells. It is equally important, however, to establish the mechanism of lipid–protein interaction and the behaviour of combined water in colloidal systems. The characteristics of the introduction of polypeptides (poly-L-glutamic acid, poly-L-leucine)[123] and a transport protein[76,77] into a liposome have been studied using Eu^{3+} and Pr^{3+} ions and ^1H and ^{31}P NMR spectroscopy. It was established that the mosaic model is applicable to bilayer vesicles. According to this model, the protein "icebergs" in the membrane float in a lipid sea. The mosaic model was also found to be applicable to blood serum lipoproteins,[124-127] the structure of which was determined by ^{13}C and ^{31}P NMR spectroscopy using Eu^{3+} ions and built-in [N–$^{13}CH_3$]-PC and -SM and 1,2-(1-oleoyl-^{13}C)-PC.[124,125] Experiments with the hexacyanoferrate(III) anion and Nd^{3+} [126] confirmed the published conclusions[124,125] that all the mobile $\dot{N}(CH_3)_3$ groups of the phospholipids in both low-density and high-density lipoproteins are situated on the external surface of the globule (Fig.12). The incomplete broadening of the ^{31}P signals in the spectra of lipoproteins in the presence of Mn^{2+} ions (80% in high-density lipoproteins and 50% in low-density lipoproteins)[127] may be due to an error in the organisation of the experiment resulting from the competition with the powerful Complexone ethylenediaminetetraacetic acid.

Mn^{2+} ions have been used to determine the location of the membrane proton of erythrocyte ghosts.[128] Comparison of the broadening of the signals in the ^1H NMR spectra of model membranes of PC

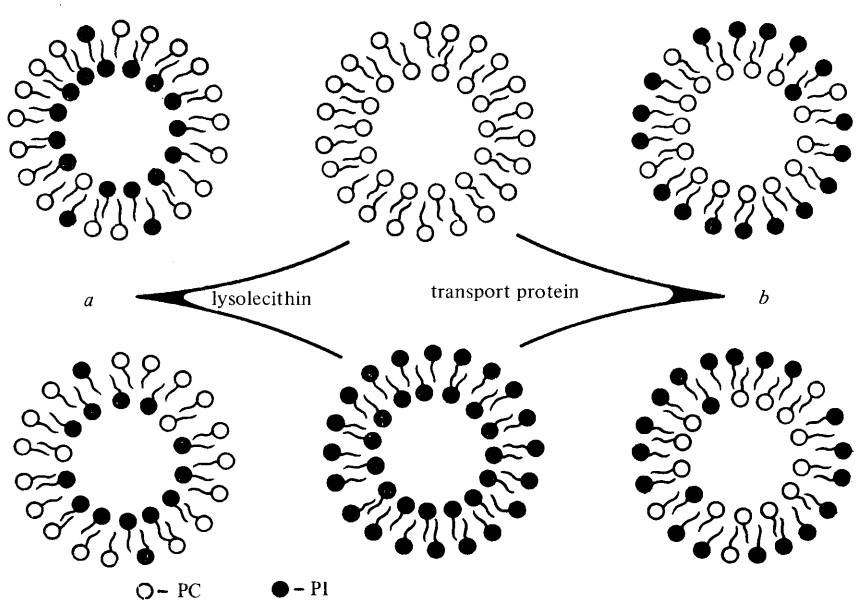


Figure 11. Diagram of inter-membrane exchange under the influence of: *a*) LPC, and *b*) a transport proteins.[53]

and the erythrocyte ghosts showed that the protein is situated on the surface of the biomembrane. This agrees with the results of an analysis of the membrane of sarcoplasm reticulum using an iminoxyl probe from its broadening effect on the ^{1}H and ^{13}C NMR signals.[129]

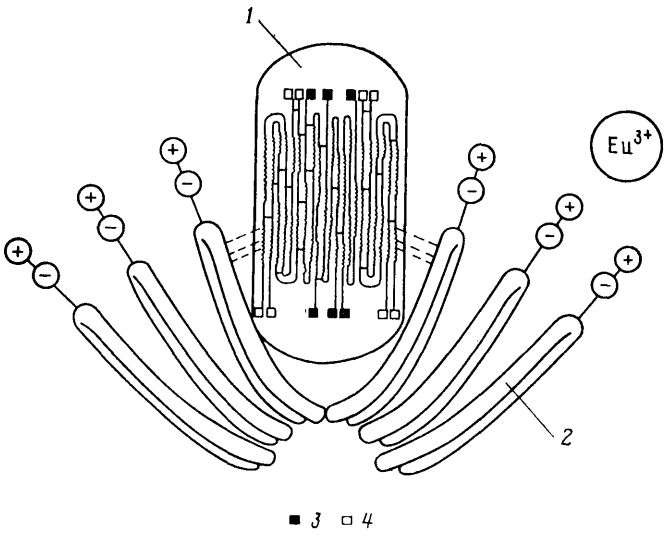


Figure 12. Model of a high density lipoprotein: *1*) protein, *2*) mixture of PC and SM, *3*) apoprotein I, *4*) apoprotein II.[125]

^{31}P NMR spectroscopy has been used[130] to measure the rate of the penetration of paramagnetic ions into heart cells. The penetration of Mn^{2+} ions made it possible to diagnose ischaemia.

Relaxation paramagnetic probes have been used many times[56-58,132,133] to study the behaviour of water in biological systems. In the first of these studies, Mn^{2+} ions were used to identify the signals from free and combined (intracellular, 4 p.p.m.) water in native rabbit sciatic nerve.[131] All other studies used similar methods. One of the most interesting is a study[132] in which NMR spectroscopy was used to investigate the intercellular transport of water in the roots of wheat plants. The introduction of Mn^{2+} ions into the space outside the cell makes it possible to eliminate from consideration the vacuolar transport of water and to control the symplast path. It is known that manganese is necessary for the liberation of oxygen in photosynthesis in the chloroplast membrane. The state of the manganese ions combined with the membrane was estimated using the values of the spin–lattice relaxation time T_1 of the protons of the water in a suspension of the thylakoid membranes of chloroplast.[133] It was shown that the manganese atoms have oxidation states II and III.

A large number of studies have been devoted to the investigation of the structure and topography of colloidal protein systems using paramagnetic hydrophilic propbes.[14,15] These studies, which are all of the same type, will not be characterised, but the results of one such study, where the possibilities provided by the method were most fully used, can be considered.[134] The authors cited used Mn^{2+}- and Cr^{3+}-ATP probes to determine the distances to different regions of carbamoyl-phosphate synthetase (CPS) by ^{1}H, ^{13}C, ^{15}N, ^{6}Li, ^{7}Li, and ^{31}P NMR spectroscopy (Table 5). These results gave the first topographical map of the environment of the substrates and the positions of the activator ions and allosteric modifiers in the CPSA dimer from *E.coli*.

Table 5. Distance from the ions Mn^{2+} and Cr^{3+}-ATP (r) to the nuclei of the ligand in the complex of CPS from *E.coli*.[134]

Mn^{2+}-ligand			Cr^{3+}-ATP-ligand		
ligand	nucleus	r, nm	ligand	nucleus	r, nm
Glu	^{13}C (5)	0.86±0.06	Glu	^{13}C (5)	0.70±0.05
$Co(NH_3)_4$-ATP	^{31}P ($\alpha\beta$); ^{31}P (γ)	0.66±0.04; 0.64±0.04	HCO_3^-; NH_4^+	^{13}C; ^{15}N	0.47±0.03; 0.74±0.05
Li^+	^{7}Li; ^{6}Li	0.75±0.04; 0.80±0.05	—	—	—

Thus the use of paramagnetic shift and relaxation hydrophilic probes combined with traditional methods of studying colloidal systems by NMR spectroscopy opens up extensive possibilities for the analysis of their structure and molecular dynamics. The results obtained by this method are of fundamental interest for establishing the mechanisms of micellar catalysis and emulsion polymerisation. The method has made it possible to study a wide range of properties of membrane systems, important both for the investigation of the molecular structure and mechanism of the functioning of cell membranes and for the development of membrane technology.

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Spectroscopy of Molecules and Molecular Complexes Dissolved in Liquefied Gases: Structure and Reactivity

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The application of the absorption spectroscopy (IR and UV) of solutions in liquefied elemental gases (N_2, O_2, Ar, Kr, and Xe) to the study of reactivities and reaction mechanisms is examined. The design of cryostats and the method of preparation of solutions are described and data on the solubilities of molecules in liquefied gases are presented. The characteristic features of the spectra of diatomic and polyatomic molecules in cryosolutions are analysed. The possibilities of the method in the investigation of unstable molecular complexes and in the elucidation of the nature of the spectra of the hydrogen-bonded complexes formed are demonstrated. The specific features of the non-linear absorption of IR radiation by molecules in the cryosolutions are discussed and a number of photochemical reactions in cryosolutions are described. It is shown that the method is promising for the solution of problems of laser chemistry in the condensed phase.
The bibliography includes 101 references.

CONTENTS

I. Introduction 730
II. Methods 730
III. The solubility of molecules in liquefied gases 733
IV. Infrared spectra of solutions of diatomic molecules 734
V. Spectra of solutions of polyatomic molecules 735
VI. Spectra of solutions of molecular complexes 736
VII. Non-linear absorption of infrared radiation and stimulation of chemical reactions in cryosolutions 739
VIII. Photochemical reactions in cryosolutions 741

I. INTRODUCTION

Liquefied noble gases are transparent in the range from the vacuum ultra-violet region to the far infrared, while liquefied oxygen and nitrogen have only weak absorption bands in the middle infrared region. For this reason, solutions of molecules in liquefied gases have been traditionally investigated by methods of absorption optical spectroscopy. The latest review devoted to the IR spectroscopy of solutions in liquefied gases was published in 1973 by Bulanin[1] and describes fairly completely aspects such as the solubility of the simplest molecules in O_2, N_2, and Ar and the design of optical cryostats. It is emphasised that the low solubility is compensated by the possibility of studying very thick layers of solutions, up to 10 metres. The review reaches conclusions about the characteristics of the IR spectra of solutions of molecules in liquefied gases: the frequency shifts relative to the frequencies in the gas phase are smaller (on average down to 5 cm^{-1}) than in any other environment, for example, in matrices; the integral band intensities are close to those in the gas phase; the widths of the bands of polyatomic molecules are usually less than 5 cm^{-1}; as a result of the narrowing of the band, the IR spectrum at 90 K contains much more information than that at low temperature in a traditional solvent, for example, in CCl_4. The presence of particular groups in the molecule, the stoichiometry of the molecule, its symmetry, and even its geometry can therefore be determined from the IR spectrum.[2]

During the last one and a half decades, numerous studies have been published in which krypton and xenon were also used as solvents. At elevated pressures (up to 50–60 atm), it is possible to carry out experiments over a wide temperature range, up to 0 °C. Naturally, this made it possible to dissolve more complex molecules, such as, for example, decamethylferrocene.[3] It became possible to investigate not only molecules but also complex formation reactions, photochemical processes, etc. Studies on the effect of laser radiation on molecules in cryosolutions began to be prosecuted on a broad front. Finally, the wave length range in which spectra are obtained has been extended—from far to near infrared and further to the vacuum ultraviolet region of the spectrum. Overall, the specific features of a simple cryosolution made it possible to obtain new information about intramolecular and intermolecular processes.

II. METHODS

It has been noted[4] that the spectroscopy of solutions in liquefied elemental gases has much in common with the familiar low-temperature matrix isolation method. However, the latter method is not suitable for the investigation of weak absorption bands because of the difficulties in the preparation of specimens with a fairly large thickness and due to the light scattering by the matrix; also this procedure does not yield quantitative information about the concentration of the impurity molecules and hence about the intensity of the spectral bands. Furthermore, the solution is in a high-pressure cell and the reacting gases cannot leave the reaction space, as happens in the matrix isolation method where the measurements are performed under high vacuum. Furthermore, in the matrix experiment there is a spectroscopic problem—the band splitting associated with the positions of the molecules in the matrix. It arises because the isolated molecules can exist in different environments in the solid matrix and the IR bands are frequently split. It is therefore sometimes impossible to distinguish the matrix splittings from spectral effects associated with changes in the molecule. The

essential feature of the method of preparation of solutions in liquefied elemental gases, including N_2 and O_2, is that the solute is introduced into a closed volume cooled as a rule with liquid nitrogen (we shall designate the word liquid by the symbol L, e.g. LN_2), and the solvent gas is condensed. Bulanin[1] described two types of optical cryostats—with horizontal and vertical optical axes. A cryostat of the second type (Fig.1), developed at the Institute of Physics at the Leningrad State University, which makes it possible to carry out experiments with thicknesses of absorbing layers up to 40 cm as a result of the double passage of the IR radiation through the solution, is particularly effective. Since the cryostat window is not in contact with the cold solution and its temperature is always close to room temperature, it can withstand high pressures (up to 60–70 atm), which permits the coverage of the temperature range 80–270 K using liquefied N_2, O_2, Ar, Kr, and Xe (Fig.2).[5]

Rebiai et al.[6] used a fairly effective design of a cryostat with a horizontal optical axis. It was made almost entirely of brass in order to reduce the effect of thermal stresses. An additional shielding chamber was placed over the chamber with the specimen. It can be filled with a cooling agent, which permits the maintenance of a constant temperature in the test solution without its boiling. The specimen chamber as well as the shielding chamber are attached to the upper lid of the cryostat via stainless steel tubes having a low thermal conductivity.

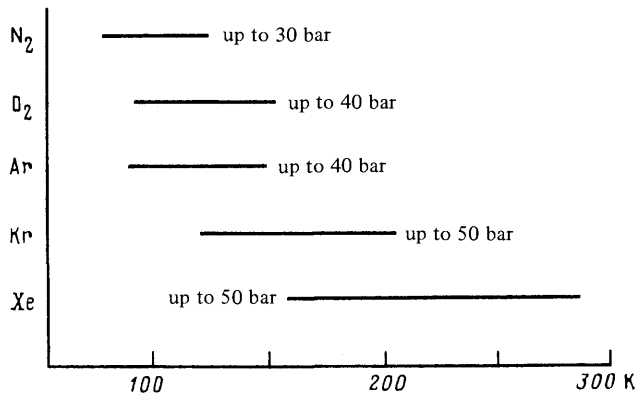


Figure 2. Region of the existence of the liquid phase of cryosolvents.[3]

In order to be able to investigate the largest possible number of substances in such solutions, their inadequate solubility must be compensated by the large thickness of the layer investigated. A novel design of multipass cell has been developed by Jeannotte and

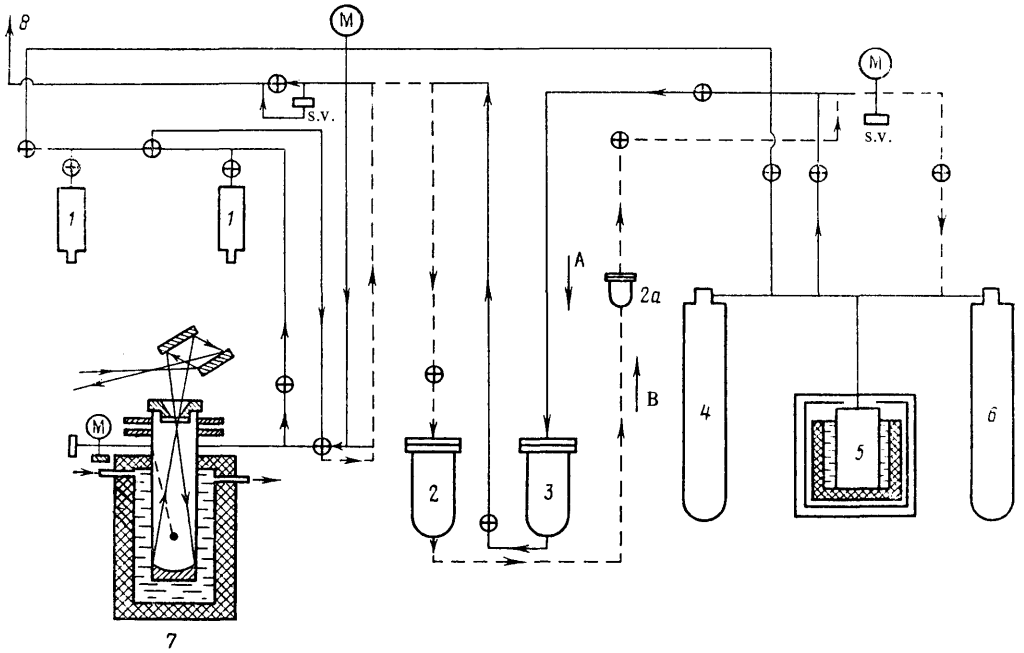


Figure 1. Schematic illustration of the apparatus for cryospectroscopy:[11] (1) vessels for the storage of the test compounds; (2), (2a), and (3) absorber systems; (4)–(6) vessels for the collection and storage of the inert gases; (7) cryostat; (8) forced evacuation; s.v.—safety valves; M—manometers; ⊕—valves; A—forward flow of the condensible gas admitted into the cryostat; B—reverse flow of the condensible gas being collected in the gas collector.

Overend.[7] The path length was varied from 0.3 to 2.1 m in 0.6 m steps. Since there are difficulties in sealing the windows under conditions where the temperature is reduced repeatedly, a cell was produced with a single window through which both the incoming and outgoing beams pass. As in the previous versions, the familiar White cell design was used. The internal 1.5 litre volume of the cell was surrounded with gaseous helium by altering the pressure of which it was possible to regulate the cooling with liquid nitrogen in the outer volume. For an optical path length of 1.5 m, LAr is entirely transparent and the transmittance of the cell over the entire IR range investigated in not less than 95%.

A design has been proposed[8] in which a change in the thickness of the optical layer by an order of magnitude is achieved without interfering with White's scheme by rotating plane illuminating mirrors placed outside the limits of the volume with the liquefied gas.

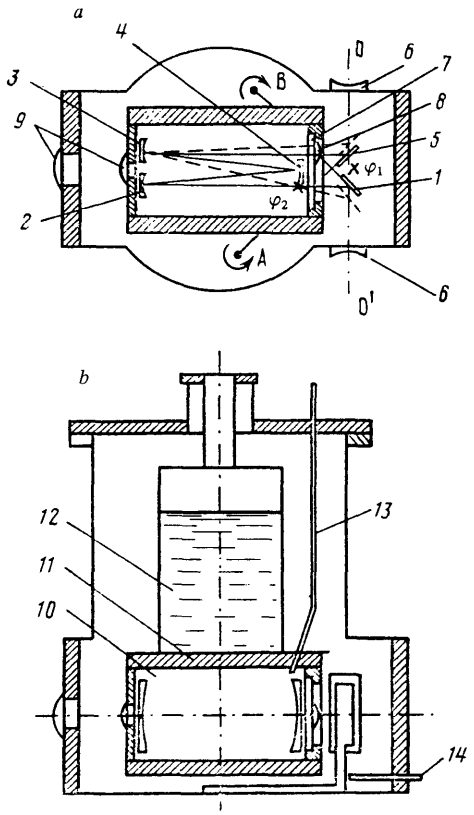


Figure 3. Schematic diagram of the cryostat:[8] (a) horizontal section: (1) and (5) plane mirrors; (2)–(4) spherical White cell mirrors; (6) scattering lenses; (7) window; (8) collector; (9) lenses; (b) vertical section: (10) cell with specimen; (11) copper jacket; (12) cooling vessel; (13) inlet for test substance; (14) component controlling the mirrors (1) and (5).

A schematic horizontal section through the cryostat with a representation of the path followed by the beam is illustrated in Fig.3*a*. The retuning of the optical scheme for two passes is achieved by rotating the plane mirror *1*, whereupon light falls immediately on the exit White cell mirror *3* (dashed line) and then, by rotating the plane mirror *5*, it is directed on to the OO' axis.

The vertical section through the cryostat is shown schematically in Fig.3*b*. The test solution is in cell *10*, which consists of a tube with an internal thread for the attachment of White cell mirrors.

Melikova[8] noted the advantages of the cryostat compared with previous designs.[1,7] Firstly, a thick optical layer is ensured for a small volume of the specimen (300 ml), achieving thereby not only economy as regards expensive solvent gases (especially xenon), but also a uniformity of temperature in the cell. Secondly, there is a possibility of adjusting the optical layer in the same specimen by an order of magnitude without the need to move any optical components in the liquefied gas. Thirdly, it is possible to work with standard spectroscopic apparatus without additional illuminating devices.

The preparation of solidified optically transparent solid solutions is of special interest, since the dissolved molecules are then in a field of known symmetry. Solid specimens, obtained by freezing liquefied noble gases, can be more crystalline than those obtained by the direct condensation of the gases. Fairly thick specimens of dilute solid solutions are sufficiently transparent for absorption spectroscopy. If the solid solutions are contained in a cell where it is possible to maintain an excess pressure of solvent vapour, the temperature can be raised up to the melting point of the solid specimen, in contrast to the matrix isolation method. The design of the corresponding cryostats has been developed by Maier.[9] In order to obtain a solid solution in xenon (it will be designated by SXe), the bottom of the cell with an optical path length of 1.3 cm is cooled to −117 °C, which is approximately 5 °C below the freezing point of pure xenon, and the top of the cell is maintained near −107 °C. Since the crystal grows upwards, the temperature of the top of the cell is slowly reduced until the crystal fills the cell. This solidification process usually lasts 4 h. The solid specimen obtained is transparent without any visible defects. Depending on the purpose of the experiment, the solid specimen is kept either several degrees below the melting point of the xenon or is cooled to lower temperatures.

Spectroscopic studies on liquid cryosystems using large optical path lengths impose extremely severe requirements on the purity of the liquefied gases.[10]

For systematic studies using expensive gases such as xenon and krypton, it is essential to make provision for a closed solvent circulation cycle (Fig.1). The purification of the gas involving the removal of the substance dissolved in the previous experiment is carried out in zeolite-filled columns and the transfer of the gas, without losses, from the cryostat to the storage compartment is achieved by recondensation in the vessel *5* cooled with liquid nitrogen.[11]

The simplest method of separation of the solutions involves the filling of the cryostat volume in the 1 : 1000 or 1 : 10 000 gas mixture, its subsequent condensation, and the addition of the solvent gas. In the measurement of the band intensities,[12] solutions of known concentration, known beforehand to be below that corresponding to saturation, were prepared by liquefying in the cryostat reference gas mixtures with the test substance.

The experiments with solutions in elemental gases are performed in the same way as those with traditional solutions. When nitrogen oxides were dissolved in LXe, the solution was constantly agitated with a magnetic stirrer, which actuated a Teflon-coated rod placed at the bottom of the cell.[13] The NO concentration in the solution depends on temperature and the NO partial presure over the

solution. In order to obtain the required concentration, an elevated NO pressure was used.

An interesting method of preparation of ozone solutions in LAr has been proposed.[14] Ozone was obtained directly in a cryostat with BaF_2 windows by irradiating LO_2 with light from a mercury lamp. The solutions in LAr were prepared by condensing AR in the cryostat after slow distillation of oxygen from a solution of O_3 in LO_2. This method makes it possible to transfer O_3 almost completely to LAr.

Cryostats with a vertical optical axis are specially convenient for the preparation of solutions of solid compounds:[3] the powder is poured into the cryostat in a stream of dry argon, the upper flange with a window is attached, argon is evacuated whilst cooling, the solvent gas condenses, and the solution is repeatedly caused to boil by releasing the pressure. One can assume that the specimen taken for the experiment dissolved if the spectrum did not change as a result of the subsequent ebullition of the solution. To accelerate the dissolution, the solution is vigorously bubbled with the gaseous medium.

III. THE SOLUBILITY OF MOLECULES IN LIQUEFIED GASES

The solubilities x of various compounds in cryogenic liquids are of independent interest for many technological problems. For example, CO_2, hydrocarbons, and NO_2 solidify during the liquefaction of air. A method has been proposed[15] for the calculation of the solubilities of solids in cryosolvents. The decisive factors in the approach described are the interaction of solute with the solvent and the melting point of the solute, its fugacity, and activity coefficient. The calculated solubilities in LO_2 [16] of different classes of compounds are given below in mole fractions (m.f.): alkanes (from methane to hexane) from 1 to 1×10^{-4}, alkenes (from ethylene to hexene) from 1 to 2×10^{-2}, acetylene 5×10^{-2}, benzene 1×10^{-4}, methanol 6×10^{-2}, CO_2 1×10^{-3}, H_2S 1×10^{-3}, NO 1×10^{-2}, NO_2 2×10^{-6}, and Kr 3×10^{-1}. The calculated solubilities of solid hydrocarbons, with the exception of methane, are higher by one and a half to three orders of magnitude than those obntained experimentally.[16] The regularities found in the solubilities of homologous series can be seen. The solubilities of alkanes and alkenes decrease with increase in molecular weight. The solubility of acetylene, which tends to form associated species, is lower than those of ethylene and isobutene. The solubilities x of olefins in LN_2 were determined by IR spectroscopy.[17] The analytical bands selected were those of ethylene ($\nu = 2168$ cm^{-1}; $\nu_{1/2} = 9.5$ cm^{-1}), propene (2034 cm^{-1}; 1.5 cm^{-1}), and but-1-ene (995 cm^{-1}; 4.0 cm^{-1}); the values of x proved to be 6×10^{-3}, 1×10^{-3}, and 1.5×10^{-4} m.f. respectively at 80 K. The solubility of olefins in LO_2 is higher by 1–4 orders of magnitude than in LN_2. Careful preparation of the saturated solution, including its bubbling with He and the measurement of the IR spectra both on heating and cooling, made it possible to determine the solubility x of linear molecules with an error in the range 15–20%: in LO_2, x is 4.3×10^{-6} for CO_2, 5.6×10^{-4} for COS, and 1.4×10^{-4} m.f. for N_2O, while x for CS_2 in LAr is 5.6×10^{-7} m.f.[18] The solubilities x of alkynes are much less satisfactorily reproducible. The following values of $10^6 x$ (in m.f.) have been obtained in LAr at 90 K: 5.4 for $HC{\equiv}CH$, 2.3 for $CH_3C{\equiv}CH$, 2.2 for $C_2H_5C{\equiv}CH$, 0.25 for $CH_2{=}CH{-}C{\equiv}CH$, and 0.16 for $HC{\equiv}C{-}C{\equiv}CH$.[19] The solubilities x of hydrocarbons containing between 5 and 8 carbon atoms in LAr have been determined[20] and have been found to lie in the range $0.3-30 \times 10^{-6}$ m.f. The parameters x in LAr and LO_2 proved to be similar. In practice this is important, since solutions in LO_2 are explosive.[4]

The values of x for certain substances have been determined from electronic absorption bands.[21] The high absorption coefficient in the UV region makes it possible to carry out measurements at lower concentrations and hence to determine x for a wider range of compounds. The list of substances and the values of x (in m.f.) found for them are as follows: 4×10^{-9} for pyrimidine in LKr, 3×10^{-10} for pyrazine in LKr, 1.4×10^{-8} and 7×10^{-10} for pyridine in LKr and LAr respectively; 5×10^{-7} for NH_3 in LAr and LKr; 5×10^{-6} and 2.2×10^{-7} for acetone in LKr and LAr; 1.1×10^{-6} for CH_3I in LAr; 7×10^{-6} and 4.5×10^{-8} for toluene in LAr and LN_2; 9×10^{-6} and 2.2×10^{-7} for benzene in LKr and LAr. A mole fraction of 2.4×10^{-3} has been quoted for I_2 in LXe.[22] Since the mole fraction x varies exponentially with temperature ($\lg x = a - b/T$), the heat of solution can be found. For the series of substances investigated, it varies from 2 to 7 kcal mole^{-1}. The solubility of toluene in LKr exceeds by more than an order of magnitude that in LAr and the solubilities of CS_2 and CH_3I in LN_2 are at least an order of magnitude lower than in LAr. Agreement between the values of x calculated by the method of Preston and Prausnitz[15] and the experimental values on the assumption that there is no interaction is achieved only for simple systems, while for solutions of toluene in LN_2, for example, the discrepancy amounts to several orders of magnitude. This makes it possible to determine the parameter characterising the interaction in solution.

Unusually high solubilities x of water in LN_2 (1×10^{-5}) and LO_2 (1×10^{-5}) have been reported.[6] Particles of ice were ground in the liquid solvent and the solution was then filtered into the cell, the degree of saturation of the solution being deterined by the intensity of the grinding. According to the authors, spectroscopic data confirm that solutions of monomolecular water were obtained. However, the frequencies quoted for the stretching vibrations of water $\nu_1 = 3605$ and $\nu_3 = 3707$ cm^{-1} are very close to those known for CO_2 in solution in LN_2 (see Section V), while the D_2O frequencies differ fairly considerably from the frequencies of this molecule in the gas phase.

In spectroscopic studies, special measurements of x frequently were not made, but the solubilities can be inferred by comparing the intensities of the IR bands and the optical path lengths. If cells 1 cm long are used, then x is as a rule higher than 10^{-3} m.f., while for cells 10 cm long the solubilities are $\sim 10^{-4}$ m.f.; smaller values of x require greater optical path lengths. Thus a solution of monomeric formaldehyde in LXe with a concentration of $\sim 10^{-2}$ m.f. has been observed in a cell 1.3 cm^{-1} long;[23] the solidification of Xe does not alter greatly the solubility x. We may note that the preparation of such formaldehyde solutions makes it possible to observe the spectra of its monomeric form, although the molecular density of CH_2O in the solution is equivalent to a vapour pressure of 30 mmHg, while in the gas phase at a pressure in excess of 4 mmHg of CH_2O, polymerisation takes place rapidly.[23] The vapour pressures of comparatively heavy molecules are usually low. Thus it is only 7 mmHg for OsO_4 and, in order to obtain the IR spectrum of the gas, it is necessary to use cells with a large optical path length. On the other hand, the intensity of the IR bands of OsO_4 in solution in LXe in a cell 2.7 cm long is equivalent to a vapour pressure of 400 mmHg, i.e. the preparation of solutions of substances with a satisfactory solubility makes it possible to achieve a high molecular density. This facilitates the analysis of molecular impurities. Thus the IR spectrum of OsO_4 shows a fairly intense ν_3 band of the isotopic form, containing ^{18}O, at a concentration of only 4×10^{-6}.[23] The

high sensitivity of the cryospectroscopic method has found practical applications in the analysis of liquefied gases, for example, of liquid O_2, for molecular impurities. The sensitivity of the absorption spectroscopic analysis of cryosolutions actually achieved at the present time has reached the level approaching a mole fraction of 10^{-10}.[4]

IV. INFRARED SPECTRA OF SOLUTIONS OF DIATOMIC MOLECULES

The changes resulting from the transfer from the gas phase to the cryosolution can be seen in relation to the IR spectra of hydrogen halides in LXe.[24] The rotational branches are well manifested in the spectra of HCl, HBr, and HI in LXe. The *Q* branch has a high intensity, as in gases under high pressure. The distance between the rotational *P* and *R* branches is greater than expected. According to the authors, this can be associated with the superposition of induced *S* and *O* branches, which are not resolved from the *P* and *R* branches in the spectrum. The selection rules characteristic of the liquid are probably associated with the anisotropic fields, which induce a shift of the *J* states. In this sense, the rotational movements of HX in LXe are assumed to be not free. One can imagine that the diatomic molecules execute unhindered rotation in the course of a significant proportion of the rotation period and that, on collisions, random changes take place in the molecular angular momentum. Frequent changes in rotation caused by collisions usually lead to the suppression of the rotational structure. Compared with the gas phase, the initial sections of the HCl, HBr, and HI bands in LXe shift by 34, 29 and 17 cm^{-1} respectively, which amounts to ~1% of the energy of the level. The strongest effect involves an increase in the integral intensity of the bands compared with the free molecule: by a factor of 2.8 for HCl, 3.1 for HBr, and 44 for HI. According to the calculation carried out by the authors,[24] the effect of the dielectric medium can explain an increase in intensity only by a factor of 1.22 and they therefore sought an explanation in terms of an increase in the amount of ionic character of HX and assume that approximately 1/16 of an electron moves from the proton to the halogen when the molecule is dissolved even in LXe. However, it follows from Iogansen's studies that the strength of the intermolecular interaction is characterised by the intensity increment, i.e. not by the ratio but by the difference of the intensities in two different states. The increments for HI and HCl are similar. The low intrinsic band intensity of free HI is the reason for the increase in its intensity by a large factor on dissolution. The relative intensities of the components depend on the solvent. Thus, whereas the *Q* branch is not manifested at all as an individual maximum in the spectrum of the HCl solution in LAr, on passing to the solutions in Kr, Xe, and O_2, its intensity increases successively. On raising the temperature, weakening of the *Q* component and the strengthening of the *P* and *R* components are observed, while the integral intensities hardly change under these conditions. The integral absorption coefficients ($\times 10^8$ in $cm^2\ s^{-1}\ mol^{-1}$) of the bands of the principal vibrational transitions of HCl in the solutions are as follows: 19.4 in the gas phase; 48 (80 K) and 34 (120 K) in LN_2; 27 (90 K) in LAr; 34 (126 K) in LKr; 53 (165 K) in LXe; 47.2 (293 K) in CCl_4.[25] Analysis of the spectra of diatomic molecules in various solvents showed that LAr and LO_2 are spectroscopically the most inert and perturb the spectra of the solutes to a minimal extent.[4]

The second moments of the bands of hydrogen halides found from the experimental data, which have a bearing on the band width, have been compared to the theoretical values. A satisfactory agreement has been obtained for solutions in noble gases, oxygen, and CCl_4, which confirms the dominant role of the rotational movement of the hydrogen halide molecules in the above systems in the formation of their absorption band contours. Thus the temperature and not the medium determines the second moments of the hydrogen halide bands in solution and liquefied noble gases or simple molecules exhibit no unusual features compared with the usual solvents. This is also seen from the integral intensities of the bands due to simple molecules. On the other hand, the solvent influences the frequencies significantly. The HCl frequency in CCl_4 (2833 cm^{-1}) is significantly lower than in LXe (2850 cm^{-1}, 200 K). Bearing in mind that the frequency depends on temperature (~2 cm^{-1} for 20 K), the frequency in LXe is very close to that in the gas phase (2861 cm^{-1}).

Chesnoy[26] investigated the IR absorption spectra, fluorescence excitation spectra, and fluorescence spectra of HCl in LXe and SXe near the melting point of xenon. The main band and overtone in the excitation spectrum have similar contours: the *Q* branch is present for the liquid phase and absent for the solid phase. However, there are also differences: the rotational structure begins to appear in the overtone for the liquid phase and the *Q* branch for the solution has a lower intensity than in the main band. The author interprets the vibrational spectrum of HCl in LXe by postulating the existence of limitations to the free rotation of HCl and by regarding them as a perturbation. The disappearance of the *Q* branch from the spectrum of the solid solution indicates a high symmetry (the presence of a centre of symmetry) of the immediate environment.

In a more careful study of the band contours of hydrogen halides in liquefied noble gases as well as liquid SF_6, discrete rotational structure of the vibrational bands has been observed not only for the transition $(0 \rightarrow 2)$[26] but also for the fundamental.[27-29] A distinctive structure has been observed in the spectrum of an HF solution in LXe in the experimental temperature range (230–250 K). Numerous rotational components are also present on the wings of the HCl band. The latter become more explicit with increase in the concentration of the solution or in the optical path length. The attempt by the authors[29] to observe the rotational structure in the spectrum of an HCl solution in LAr failed, although the purely rotational absorption was observed for this solution in the long-wavelength IR spectrum.[30] The first resolved lines in both the near and far infrared components of the spectrum of the HCl solution in LKr corresponded to $J = 4$. The frequency shifts of the rotational components as a function of the density of the medium in the purely rotational spectra are appreciably smaller than in the vibrational-rotational spectra, which apparently reflects the contribution by the vibration. The linear variation of the shift as a function of the density breaks down on passing from the gas to the liquid phase, the shift becoming much greater. The widths of the purely rotational bands of HCl in LKr and LXe are 3 cm^{-1},[30] which means that they are several times narrower than the rotational components of the vibrational band.[29] The broadening of the rotational components in LAr is in fact most likely to prevent the manifestation of the fine structure of the spectrum. The results of the above study[29] have shown that the vibrational and rotational relaxation processes, which determine the band widths, exhibit different dependences on the density and that the rate of rotational relaxation increases to a greater extent for densities corresponding to the liquid solvent.

We confined ourselves to describing, as an example, the characteristic features of the spectra of solutions of hydrogen halides and in the following sections we shall also present data on the spectra of solutions of other diatomic molecules: CO, NO, H_2, N_2.

V. SPECTRA OF SOLUTIONS OF POLYATOMIC MOLECULES

1. Infrared Spectra

The rotation of polyatomic molecules such as CO_2, SF_6, etc., placed in cryosolution, is greatly inhibited by collisions with their environment, whilst their rotational movement is best described as diffusion. This results in a considerable narrowing of the vibrational-rotational contour of the band compared with that observed in the gas phase and greatly simplifies the IR spectra. The low temperature of the solutions in the cryosolvents and their great inertness lead to further narrowing of the spectral bands and a decrease in their overlap. This makes it possible to determine not only the frequencies of the principal vibrational transitions but also those of overtones and combination bands. In such solvents, it is also easier to measure the absolute and relative band intensities and isotope effects. At low temperatures, a significantly greater proportion of molecules are in the vibrational ground state, especially in the absence of low frequencies in the spectrum, and the interpretation of the spectrum becomes simpler as a result of the weakening of the bands due to hot transitions. The spectroscopy of cryosolutions of polyatomic molecules is a valuable research technique especially in those cases where the rotational fine structure of the vibrational band cannot be resolved in the gas phase.[12,31] Initially we shall present the results of the study of the IR spectra of solutions of the triatomic linear molecules CO_2, COS, CS_2, and N_2O in cryosolvents,[12] which clearly demonstrates the great possibilities of the method.

The following bands can be observed in the spectra of CO_2 dissolved in LO_2: 665 cm^{-1} (Π_u, ν_2), 2343 cm^{-1} (Σ_u, ν_3), 2277.5 and 3702.5 cm^{-1} (Σ_u, $\nu_1 + \nu_3$) and 3601.2 cm^{-1} (Σ_u, $2\nu_2 + \nu_3$). The weak 2277.5 cm^{-1} band, located near the most intense ν_3 band, corresponds to the isotopic modification $^{13}C^{16}O_2$. The relative intensity of these bands is consistent with the natural abundance of the ^{13}C isotope (1.13%). Since the 3601.2 and 3702.5 cm^{-1} bands are components of the Fermi resonance, the distance between the non-interacting levels $\Delta = 28.4$ cm^{-1} was determined from the ratio of the relative intensities:

$$\nu_1 + \nu_3/2\nu_2 + \nu_3 = \frac{\varkappa + \Delta}{\varkappa - \Delta}$$

($\varkappa$ is the observed distance between the interacting levels); under these conditions, the $10^0 1|W|02^0 1$ perturbation matrix element is 49.1 cm^{-1}, which agrees well with the value obtained for the gas.

The higher solubility of COS in LO_2 made it possible to record almost all the second- and third-order bands corresponding to transitions to non-degenerate levels. Fourth-order bands have also been observed: $4\nu_2$ and $2\nu_1 + 2\nu_2$. At 90 K, it is possible to observe a series of absorption bands in the spectrum of the COS solution which can be attributed to isotopic modifications with the ^{13}C, ^{18}O, and ^{34}S isotopes. The isotopic splittings calculated in terms of the harmonic approximation are close to the observed splittings and the relative intensities agree with the abundances of the isotopes within the limits of the error.

Comparison with the gas phase spectra shows that, on passing to the solution, the vibrational frequencies undergo a bathochromic shift. The maximum shift, reaching 9 cm^{-1} for COS, is observed for the ν_3 stretching vibration bands, which have the highest intensity. The shift of the overtone bands and combination bands is approximately equal to the sum of the shifts of the individual levels. It has been stated[12] that, in determining the anharmonic potential energy terms, the spectra of cryosystems make it possible to obviate the difficulties associated with the separation of the vibrational and rotational motions and the allowance for the vibrational-rotational interactions.

The absolute intensities (integral absorption coefficients) of the $\nu_3(CO_2)$ and $\nu_1(N_2O)$ bands have been measured in the spectra of solutions in LO_2. The observed values $A(\nu_3) = (35 \pm 2) \times 10^{-7}$ cm^2 s^{-1} and $A(\nu_1) = (29.5 \pm 1.0) \times 10^{-8}$ cm^2 s^{-1} do not differ from the data for the gas phase within the limits of the scatter of the literature values. Owing to the smallness of the refractive index of liquid oxygen ($n = 1.22$), the correction of Polo and Wilson, which takes into account the influence of the solvent on the absorption coefficient, is about 10%, i.e. does not exceed the error of the measurements of the band intensities in the spectra of gases.

The data obtained by Bertsev et al.[12] provide for the first time the initial information for a large number of compound and overtone bands essential for a rigorous formulation of the electro-optical problem.

Despite the inertness of LXe, the latter induces the (02^20) CO_2 transition with a frequency of 1324 cm^{-1} as a consequence of its interaction with CO_2.[10]

In connection with the study of the selective action of laser radiation on matter, there has recently been a growth of interest in the determination of data concerning the highest vibrational state of polyatomic molecules.[32] A reliable interpretation of the structure of the IR spectra of CF_3I involves considerable difficulties because of the existence of several low-frequency fundamental vibrations of this molecule. At room temperature, about half of the CF_3I molecules are in excited states, so that a series of bands due to hot $\nu_i \rightarrow \nu_k + \nu_i$ transitions are superimposed on each absorption band. The results of the study of the IR absorption spectrum of a solution of CF_3I in LAr at 90 K in the frequency range 200–4000 cm^{-1} have been published.[33] The frequencies, half-widths, and relative integral intensities of 70 vibrational bands have been determined and interpreted. The doublet in the region of 530 cm^{-1} has been interpreted as due to the Fermi resonance of two vibrational states, ν_5 and $2\nu_6$, which lead in its turn to the appearance of several other Fermi diads, namely ($\nu_5 + \nu_6$, $3\nu_6$), ($\nu_2 + \nu_5$, $\nu_2 + 2\nu_6$), ($\nu_3 + \nu_4$, $\nu_4 + 2\nu_6$) [This should be ($\nu_3 + \nu_5$, $\nu_3 + 2\nu_6$) or ($\nu_4 + \nu_5$, $\nu_4 + 2\nu_6$) (Ed. of Translation)], and ($\nu_2 + \nu_4 + \nu_5$, $\nu_2 + \nu_4 + 2\nu_6$). For the pairs of states enumerated above, the matrix elements of the interaction depend on the same cubic constant K_{566} in the expansion of the potential energy of the molecule in series in terms of the normal coordinates, the average value of the constant being $K_{566} = 9.0 \pm 0.1$ cm^{-1}. The resonance of the four fully symmetrical states ν_1, $2\nu_5$, $\nu_5 + 2\nu_6$, and $4\nu_6$, the matrix elements of the interaction of which are determined by the two cubic constants K_{566} and K_{155}, has also been observed. The cubic constant $K_{155} = 4.6$ cm^{-1} has been estimated. Certain anharmonicity constants have been found from the vibration band frequencies with a unique interprettion (in cm^{-1}): $X_{22} = -0.2$; $X_{23} = -1.6$; $X_{33} = -1.0$; $X_{24} = -6.3$; $X_{34} = -0.2$; $X_{25} = -1.0$; $X_{36} = -0.3$; $X_{26} = -0.5$; $X_{44} = -6.8$; $X_{56} - g_{56} + r_{56} = -3$; $X_{66} = 0.7$; $g_{66} = 0.2$; $g_{44} = 4.1$; $X_{46} + g_{46} = -0.9$. The analysis of the CF_3I spectrum at a low temperature led to the conclusion that the real band structure of the gas phase at room temperature is very complex. The spectrum in the region of the $\nu_1(CF_3I)$ vibration, in resonance with the radiation of the CO_2 laser with the aid of which it is possible to perform the selective dissociation of CF_3I with formation of the CF_3 radical is of special interest. The results of the study of Bulanin et al.[33] have shown that the number of energy states involved in the anharmonic interaction

increases rapidly with increase in the quantum number v_1 and, furthermore, transitions to degenerate states, among which the $v_1 + 2v_5$ transition should be the source of the intensity, are superimposed on the same region. Thus the strong interaction of the v_1, v_5, and v_6 vibrational modes combined with the low anharmonicity constants leads to the formation in the CF_3I spectrum of energy zones with a high density of states, promoting an effective excitation of this molecule by the laser radiation up to the dissociation limit.[33] The IR absorption spectra of $^{12}CH_4$ and $^{13}CH_4$ in solution in LAr have been interpreted similarly.[34]

The simultaneous IR transition, arising from $v_3(SF_6)$ and the fundamental O_2 vibration in SF_6 solution in LO_2 at 78 K, has also been observed.[35] The frequency of the 2490.6 cm^{-1} band is independent of the SF_6 concentration, while the absorption coefficient and the band half-width increase linearly with increase in the SF_6 concentration. The calculated frequency, obtained by adding together $v_3(SF_6)$ and the intrinsic frequency of O_2, is 2492.1 cm^{-1}. The observed value differs somewhat from the calculated ones since the latter are based on binary interactions and the low gas pressure limit, which are not fully legitimate for solutions in liquids.

The spectra of not only organic but also organometallic compounds in cryosolvents have been interpreted.[36] The structure of a molecule such as $Ru(CO)_5$ has not been reliably established from the IR spectra either in solution in n-hexane or on matrix isolation of solid N_2 even in the study of the ^{13}CO-enriched compounds, since the IR spectrum of the solution always consists of two broad bands and the complex character of the spectrum of the matrix-isolated $Ru(CO)_5$ is due to the matrix splitting. The IR bands of the $Ru(CO)_5$ dissolved in LXe at -60 °C are narrowed. Thus $v_{1/2}$ for the a_2'' band of the solution in LXe is 2.0 cm^{-1}, while that of the solution in n-hexane is 6.8 cm^{-1}. In the IR spectrum of $Ru(CO)_5$ enriched in ^{13}CO to the extent of 26.5%, 16 bands have been observed. The monosubstituted specimen, containing ^{13}CO in the equatorial position, should have the comparatively low C_{2v} symmetry and all its bands should be resolved in the IR spectrum. Gregory et al.[36] assigned the following bands to this isotopic specimens: a_1—2120.7 cm^{-1}, b_2—2038.9 cm^{-1}, a_1—2032.2 cm^{-1}, b_1—2001.6 cm^{-1}, and a_1—1964.0 cm^{-1}. The overall character of the $Ru(CO)_5$ spectrum is fully consistent with the D_{3h} molecular symmetry. The presence of 16 frequencies made it possible to determine all the force coefficients of $Ru(CO)_5$ (in N m^{-1}): K_{ax} = 1728.38; K_{eq} = 1653.28; $K_{ax,eq}$ = 27.57; $K_{eq,eq}$ = 34.82; $K_{ax,ax}$ = 48.09. The band intensities in the spectrum of $Ru(CO)_5$ in LXe have been calculated in terms of the local C—O dipole approximation, the results being in good agreement with experiment. The spectrum of ferrocene in solution in LXe has been interpreted similarly.[37]

Holland et al.[9] published IR spectra demonstrating the isotopic splitting of the BCl_3, SeF_6, OsO_4, MoF_6, and $TiCl_4$ bands in solid solutions and carried out a comparison of the results obtained in sputtered matrices, in the gas phase, and in liquid solutions. As an example, we may quote the data for BCl_3. In SKr (116 K) and SAr (84 K), the BCl_3 spectrum contains narrow bands of the split v_3 vibration and the doublet due to the degenerate v_3 vibration, which can be unambiguously assigned to $^{10}B^{35}Cl_3$ (983.2 and 985.6 cm^{-1}) and $^{11}B^{35}Cl_3$ (944.6 and 947.0 cm^{-1}) respectively. The frequencies of these bands decrease with decrease in temperature by approximately 0.04 cm^{-1} K^{-1} and can readily coincide with the CO_2 laser lines in the study of its selective action on BCl_3. Comparison with the gas phase spectrum indicates a much greater information content: $v_3(^{11}BCl_3)$ has 7 components in the solid phase and only two in the gas phase.

2. Ultraviolet Spectra

The influence of the solvent on the UV spectrum of the molecules has been demonstrated in relation to the $^1\Sigma_g^+ \leftarrow {}^1\Sigma_g^+$ absorption band of carbon disulphide in four solvents.[38] Compared with the solution in LAr, the band in LN_2 has undergone a hypsochromic shift by 75 cm^{-1} and the maximum of the continuous background envelope reaches 40% of the band maximum (instead of the 30% for the solution in LAr at the same temperature); consequently the vibronic maxima are broadened to a greater extent. The pattern for the solution in LXe is completely different: the band is very diffuse and its maximum has undergone a bathochromic shift by 1200 cm^{-1} and is located in approximately the same position as for the solution in hexane at room temperature. The complete disappearance of the vibronic structure in solution in hexane and its partial retention in LXe are noteworthy. This explains the possibility of the selective action of UV radiation on certain molecules dissolved in LXe and other elemental liquefied gases but not in molecular liquids. Clearly, from the standpoint of selectivity, LAr and LN_2 are preferable to LXe.

The vibronic structure of bands in the spectra of solutions in liquefied elemental gases is not retained for all molecules. Thus, on passing to the condensed phase, the vibronic band structure in the spectrum of acetone in the region of 195 nm becomes completely diffuse, the band positions being virtually the same in LAr, LXe, and hexane. Marked broadening of the vibronic components also occurred after the addition of gaseous Ar at a pressure of 130 atm. Such behaviour of the 195 nm acetone band shows that the upper state of this transition is mixed: Rydberg orbitals are also involved in it. Overall, the use of cryosolutions for the investigated $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands for a large series of compounds makes it possible to improve significantly the resolution of the fundamental vibrational structure.[39] On the other hand, although most of the structure characteristic of the gas is retained in the UV spectrum of OsO_4 solution in LXe,[23] it is also retained in other solvents (Ar, Kr, N_2O, CH_4, C_5H_{10}, CF_4, CF_3Cl, and BF_3). The frequencies of the band maxima are displaced by 2—10 nm compared with the spectrum of the gas phase, the shift depending on the type of solvent.

Fine structure has not been observed in the UV spectrum of CH_2O in the vapour phase, and the width of the spectral bands for the cryosolution is somewhat greater. Nevertheless, the UV spectrum of the CD_2O solution shows a major isotope shift compared with CH_2O used for the photolytic isotope separation.[23]

The vibronic structure of the ^1L_b absorption band of benzene dissolved in liquefied Ar (from 138 to 148 K), CF_4 (from 151 to 190 K), and Kr (from 122 to 160 K) has also been investigated.[40] Since the vibronic components of the band in the argon and Freon solutions are fairly narrow, while the majority of the "hot" transitions are frozen, it is possible to carry out a detailed analysis of the vibrational band structure and to refine the assignment of certain vibronic components.

VI. SPECTRA OF SOLUTIONS OF MOLECULAR COMPLEXES

The low temperature which can be attained in liquid elemental gases should permit the observation, under the conditions of infinite dilution, of the association of molecules which does not occur under

the usual conditions because the initial components are gases and the complex formation constant is small. The high inertness of liquefied noble gases is of decisive importance for the synthesis of weak complexes. The interaction of dissolved molecules with the environment under these conditions is significantly weaker than in traditional solvents. Naturally the components of the complex must dissolve effectively in the cryosolvent. By selecting the concentrations of the initial molecules, it is always possible to achieve a situation such that the equilibrium in the complex formation process can be observed under the experimental conditions and by altering the temperature its influence not only on the spectroscopic characteristics but also on standard thermodynamics can be determined.

The first study of this kind[41] dealt with the investigation of the system comprising $CHF_3(CDF_3)$ and $N(CH_3)_3$ in LAr and LKr. When the amine was added to the CHF_3 solution, the intensity of the ν_1 (3038 cm^{-1}) and ν_4 (1373 cm^{-1}) bands diminished and the bands disappeared in the presence of a large excess of the amine and were replaced by two other bands, at 3016 and 1404 cm^{-1}, which are associated with the corresponding vibrations in the hydrogen-bonded complex (HBC). The equilibrium constants of the association process in the temperature ranges 90–130 K for LAr and 120–160 K for LKr as well as the thermodynamic parameters $\Delta H^0 = 3.5 \pm 0.2$ kcal mol^{-1} and $\Delta S^0 = 15 \pm 2$ cal mol^{-1} K^{-1} were determined from the integral intensities of the ν_1 and ν_4 bands for CHF_3 and the ν_1 band for CDF_3. We may note that in the matrix isolation method the frequencies of the complex frequently cannot be obtained and the equilibrium cannot be observed. Studies on the HBC in cryogenic solutions have been prosecuted in two directions. The first[42,43] dealt with the study of the parameters of the bands of weak complexes which as a rule do not exist under the usual conditions. By virtue of the inertness of the liquefied noble gases, interactions which occupy an intermediate position between typical van der Waals interactions and a weak hydrogen bond can be studied in them. In the second direction,[11,43] the influence of the cryogenic solvent on the spectroscopic characteristics of moderately strong HBC, whose spectra are known both in the gas phase and in a traditional solvent, was investigated.

The results of measurements of the HCl, DCl, and HBr spectra in mixed solvents consisting of LAr with added N_2 or CO have been described.[42,44] In these systems, a narrow symmetrical band appears against the background of the broad band characteristic of solutions of hydrogen halides HX in LAr (see Section IV). The narrow band was assigned to the complexes of hydrogen halides with N_2 or CO, the intensity of the bands due to the free HX molecules decreasing with increase in the N_2 and CO concentrations. Thus, whereas HCl in LAr has a band at a frequency of 2869 cm^{-1} with a half-width of ~ 100 cm^{-1}, for the $HCl-N_2$ complex the frequency is $\nu = 2864$ cm^{-1} and $\nu_{1/2} = 11$ cm^{-1} and for the HCl–CO complex the frequency is $\nu = 2835$ cm^{-1} and $\nu_{1/2} = 9$ cm^{-1}. The narrowing of the HX bands has been explained by the rotation being hindered due to the greater moment of inertia in the complex. Complex formation influences the spectra of the molecules in the gas phase in a similar manner. The spectral parameters show that the interaction of the above diatomic molecules is local. The interaction between CCL_4 and HCl in LXe and LKr turns out to be similar. A narrow band appears in the IR spectrum at ~ 2840 cm^{-1} and it may be that it is in fact the local interaction which determine the contour of the HCl band in liquid CCl_4.[44]

Wek complexes of proton donors such as HBr, HF, $HC\equiv CH$, $CH_3C\equiv CH$, and HCN have also now been investigated.[45,46] the same behaviour has been observed as for the HCl complexes.

The complexes of olefins with HCl were classified as thermally unstable systems or systems unstable as regards their reaction (for example, with isobutene). Cooling to LN_2 temperatures makes it possible to investigate these complexes either as a result of suppressing the reaction or due to a sharp increase in the complex formation constant. The shift of the HCl bands on going from the complex with eithylene to that with trimethylethylene increases from 100 cm^{-1} to 260 cm^{-1}.[47,48] If the first can be assigned to weak HBC, then the second is due to moderately strong HBC. Together with the bathochromic band shift, another property of the band due to the HCl in the HBC is its higher intensity, by more than an order of magnitude compared with free HCl. The complex formation constants were determined at 77 and 95 K. The ΔH were calculated for this temperature range from the van't Hoff equation (Table 1). It was found that the experimental results satisfy well the relations between ΔH and $\Delta A^{1/2}$ and between ΔH and $\Delta\nu$, especially the latter. Thus the spectroscopic characteristics observed in the complex formation process make it possible to classify the complexes between HCl and olefins as typical HBC and to conclude that the interaction proceeds via the hydrogen atom. The entropy ΔS of complex formation amounted to 11 cal mol^{-1} K^{-1}. These characteristics of the olefin–HCl complexes in solution in LN_2 were found to be close to those obtained later[49] in solution in LAr: ν(HCl) = 2774 cm^{-1}, $\nu_{1/2} = 15$ cm^{-1}, and $\Delta H = 1.5 \pm 0.1$ kcal mol^{-1} for C_2H_4-HCl, ν(HCl) = 2732 cm^{-1} and $\nu_{1/2} = 20$ cm^{-1} for C_3H_6-HCl, and $\nu = 2679$ cm^{-1} and $\nu_{1/2} = 28$ cm^{-1} for C_4H_8-HCl. The HCl frequency is also somewhat higher for the solution in LAr compared with that in LN_2 and the band half-width is somewhat smaller.

Table 1. Parameters of the IR spectra and the enthalpies of complex formation for HCl–olefin systems in solution in liquid N_2.[47]

Proton acceptor	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	$\nu_{1/2}$, cm^{-1}	$10^{-4}A$, litre mol^{-1} cm^{-2}	K_p(77 K), litre mol^{-1}	K_p(93 K), litre mol^{-1}	ΔH, kcal mol^{-1}		
							authors data (Ref. 47)	calc. from ΔA	calc. from $\Delta\nu$
—	2870	—	—	0.4	—	—	—	—	—
Ethylene	2770	100	25	2.2	30	8	1.4	2.3	1.6
Propene	2720	150	35	2.7	$3.2\cdot10^2$	35	2.2	2.7	2.2
Isobutene	2660	210	30	3.4	$1.5\cdot10^3$	$1.3\cdot10^2$	2.6	3.5	2.7
Trimethylethylene	2610	260	30	4.3	$3\cdot10^3$	$6\cdot10^2$	3.5	4.1	3.2

The data for complexes of HCl with olefins in solution permit a more correct comparison of the electron-donating properties of olefins and aromatic compounds, especially since the frequency of HCl (2685^{-1}) in the complex with hexamethylbenzene was determined in solution in LXe.[50] Comparison of the frequencies of the complexes with trimethylethylene and hexamethylbenzene shows that the decrease in frequency for the olefin is greater despite that the fact that its ionisation potential is higher (8.67 eV) than that of hexamethylbenzene (7.85). An intermediate case obtains for complexes of ferrocene and its methyl derivatives with HCl.[3]

Whereas the small width of the band of HCl in the weak C_2H_4-HCl complex is understandable, the fact that the band of the moderately strong $(CH_3)_2=CHCH_3-HCl$ complex remains narrow despite its significantly greater shift is unusual. This result led to the hypothesis that the marked broadening of the stretching vibration bands of the XH bond, observed in traditional solvents, is

not a universal property of the hydrogen bond but depends on the nature of the solvent. A study was therefore made in LKr and LXe of a series of HBC whose parameters were known for traditional solvents.

We selected the $CH_3CN-HCl$ complex as the principal object of study because of its adequate stability and high symmetry.[51] According to literature data, the HCl band half-width for the solution of this complex in CCl_4 is 275 cm^{-1}, while for the solution of HCl in CH_3CN it is 350 cm^{-1}. On the other hand, the spectrum of the gas phase complex consists of the principal HCl band with a half-width of 100 cm^{-1} and a weaker difference band, separated from the principal band by ~ 100 cm^{-1}. The band half-width for the HCl in the complex was estimated as ~ 70 cm^{-1} in solution in LXe ($T \simeq 165$ K) at HCl and CH_3CN concentrations of 3×10^{-4} and 6×10^{-3} M respectively,[51] i.e. much lower than in solution in CCl_4 and somewhat lower than in the gas phase. An even smaller value of $\nu_{1/2}$ (HCl) = 40 cm^{-1} has been obtained by Muradov and Tokhabze for $CH_3CN-HCl$ in solution in LXe.[44] The study of this complex in LKr showed that the HCl band becomes narrower ($\nu_{1/2} \simeq 35$ cm^{-1}) at the same temperature (165 K) and that cooling of the solution in LKr from 165 to 130 K leads to further narrowing of the band to 30 cm^{-1}. These data have been confirmed.[44] Thus cooling (from 290 to 130 K) and the change of solvent (from CCl_4 to LKr) narrowed the ν(HCl) band for the $CH_3CN-HCl$ complex by an order of magnitude. Previously this effect was not known. Subsequently, using CD_3CN and higher concentrations of the $CD_3CN-HCl$ complex,[11,43] it was possible to obtain for the solution in liquid Xe the overall and difference ν(HCl) $\pm$ ν_σ frequencies, where ν_σ is the frequency of the stretching intermolecular vibration of the hydrogen bond. This is a consequence of the narrowing of each band.

Table 2. The frequencies and widths of the ν(OH) bands of the binary hydrogen-bonded complexes in various media.[53]

T, K	Medium	$(CF_3)_3COH-CD_3CN$		$(CF_3)_3COH-(CD_3)_2O$	
		ν, cm^{-1}	$\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	$\nu_{1/2}$, cm^{-1}
300	gas	3355	70	3190	120
	CCl_4	3250	160	3090	220
	Freon	3245	160	3100	200
270	xenon	3285	65	3135	130
	Freon	3235	160	3085	195
250	xenon	3280	65	3130	130
	Freon	3230	160	3075	185
200	krypton	3290	45	3140	115
	xenon	3270	50	3125	120
	Freon	3190	155	3055	180
150	krypton	3275	40	3127	110
	Freon	3150	150	3030	180
125	krypton	3270	35	3120	105
	Freon	3150	150	3010	180

In order to discover how general is the narrowing of the ν(XH) band on passing to an atomic solvent, a study was made[52] of a large number of heterocomplexes of methanol, trifluoroethanol, and perfluoro-t-butyl alcohol and their deuterio-derivatives with representatives of various classes of bases—olefins (C_3H_6), nitriles (CH_3CN), ethers [$(CH_3)_2O$], sulphides [$(CH_3)_2S$], ketones [$(CH_3)_2CO$], and amines [$(CH_3)_3N$] in solution in LXe and LKr in the temperature range 120–270 K. The ν(OH) frequency shifts from 70 to 500 cm^{-1} compared with the free alcohol, i.e. both weak and moderately strong complexes were investigated. Comparison with literature and own own[53] data shows that the ν(OH) band widths for the complexes of these alcohols in solution in the usual molecular solvents are greater by a factor of between 2 and 4 than in the atomic solvent at the same temperature (Table 2). On the other hand, the ν(OH) band widths of a gas-phase complex and the complex in LXe are approximately the same. Furthermore, the ν(OH) band widths of the complexes in solution in LXe and LKr are virtually the same in the same temperature range, which implies that the difference between the macroscopic parameters of the atomic solvents has little influence on the band width.

The influence of the solvent on the ν(OH) frequency is noteworthy: for all the complexes investigated, the frequency in LXe at 250–270 K is lower by 40–70 cm^{-1} than in the gas phase and higher by 30–40 cm^{-1} than in solution in CCl_4. In LKr, the ν(OH) frequency is higher by 10–20 cm^{-1} than in LXe at the same temperature.

The parameters of the ν_σ band, due to the intermolecular vibration of the (A...B) hydrogen bond itself, which is located in the far infrared, have also been investigated for a series of complexes of HCl with fluoro-alcohols in LXe and n-pentane at identical temperatures (165–250 K).[54,55] The band width proved to be ~ 30 cm^{-1} and was independent of the type of solvent. Such different types of influence of the atomic solvent on the ν(XH) and ν_σ band widths can be described by the theory developed by Sakun.[56] According to this theory, the broadening of the above band is due to different factors. The ν_σ band is formed under the influence of the oscillatory component of the motion of the A...B bond, while the width of the ν(XH) band and its structureless character are determined by the dissipative component of the A...B mode. The approximate equality of the ν(XH) band widths of the HBC in liquid noble gases and in the gas phase at similar temperatures indicates a weak interaction of the HBC with the atomic solvent. Presumably, in the atomic solvents, as in the gas phase, the ν(XH) band width is determined mainly by the contribution of the "hot" transitions of the ν_β deformation vibration. The principal difference in band shape should be the "smearing out" of the fine structure of the spectrum by the solvent. A decrease in temperature in LXe and LKr leads to the partial freezing out of the "hot" transitions and a decrease in their contribution to the ν(XH) band width with a temperature contaction coefficient of 0.1–0.3 cm^{-1} K^{-1}. More intense cooling, which is attainable in the matrix isolation method, leads to the almost complete freezing out of the "hot" transitions and in certain cases to a sharp narrowing of the band. For example, the width of the ν(OH) band of the complex of perfluoro-t-butyl alcohol with acetonitrile in the Ar matrix is only 10 cm^{-1}.[57] The observed temperature-induced shift of the ν(OH) band of the HBC investigated in LXe and LKr is 0.1–0.3 cm^{-1} K^{-1} and can be caused by a change in the contribution of the "hot" transitions as a result of cooling and hence a redistribution of the intensities within the limits of the band. the presence of the narrow ν(OH) and ν(OD) bands in the spectra of the series of complexes investigated made it possible to measure with a high degree of accuracy the isotope ratio, whose value for both weak and moderately strong HBC proved to be approximately equal to that for the free alcohol. The results obtained show that the isolated HBC do not exhibit an anomalously high anharmonicity. It is noteworthy that narrow ν(XH) bands are not always obtained in LXe and LKr, fairly broad bands remaining in the spectra of the complexes of acetone[50,52] and polymeric methanol.[50,58] Their width

can apparently be accounted for either by the presence of complexes of different composition or by their different structures.

The presence of a narrow ν(XH) band in the spectrum of the LXe solution made it possible to consider the problem of the site of coordination of HCl or perfluoro-t-butyl alcohol in complexes with a series of metallocene derivatives ranging from ferrocene to decamethylferrocene.[3,59] In principle, there is a possibility of coordination of both to the ring and to the metal atom. In both cases, the presence of only one ν(XH) band, displaced to lower frequencies, indicates the formation of a hydrogen-bonded complex of one type. the values of Δν and Δν for the interaction of ferrocenes with $(CF_3)_3COH$ are somewhat higher than for the interaction with HCl owing to the somewhat greater proton-donating capacity of the alcohol. In view of the similarity of the results for the HCl complexes with ferrocene,[3] olefins,[42,47] and aromatic compounds,[50] one can assume that the hydrogen bond is formed with the cyclopentadienyl ring and not with the metal atom. The same type of coordination is characteristic of the $(CF_3)_3COH$ complexes.

For carbonyl-containing cyclopentadienyl metal complexes, there are as many as three possible centres for the formation of a hydrogen bond: the π-ligand, the metal atom, and the oxygen atom of the CO group. When $(CF_3)_3COH$ is added to a solution of $CpMn(CO)_2$. .$P(iso\text{-}Pr)_3$ in LXe at 180 K, a band appears at 3415 cm^{-1}, indicating the formation of a HBC, in addition to the 3590 cm^{-1} free alcohol band.[60] The identification of the type of coordination was made on the basis of the changes in the region of the CO vibrations. The IR spectrum of a solution of $CpMn(CO)_2P(iso\text{-}Pr)_3$ in LXe contains bands at 1935 and 1873 cm^{-1}, while in the spectrum of its complex with alcohol the bands are shifted to 1931 and 1835 cm^{-1}. On the basis of the bathochromic shift of ν(CO), Lokshin et al.[60] concluded that the oxygen atoms of the carbonyl groups are involved in the hydrogen bond. When the spectrum at 180 K was subtracted from the spectrum at 165 K, two further bands become visible at 1906 and 1832 cm^{-1}; they have been assigned to a 1:2 complex in which two alcohol molecules interact with both CO groups.

Low temperatures make it possible to study also the intermolecular interaction of simple molecules, for example, those of NO and NO_2, in LXe.[13,61] In addition to the band due to the free molecule, a band at 1762 cm^{-1}, due to $(NO)_2$, appears in the spectrum of the NO solution and a band at 3594 cm^{-1} has been assigned to a combination band of the dimer. The authors were unable to conclude which form, *cis*- or *trans*-, of ON−NO exists in LXe. When NO_2 was dissolved in LXe, N_2O_4 bands were clearly manifested: at 375, 422, 743, 1251, and 1742 cm^{-1}; a large number of bands due to the combination vibrations of N_2O_4 were also observed. The authors suggest that only a planar conformation of N_2O_4 with D_{2h} symmetry exists in LXe between 163 and 233 K. One of the bands, at 1813 cm^{-1}, may be due to the asymmetric form $ONONO_2$, which has been identified in the IR spectrum of solid N_2O_4. According to spectroscopic and photolytic data, N_2O_3 exists in the form of two isomers: $ONNO_2$ and ONONO. In the spectrum of the solution of NO and NO_2 in LXe, the IR bands of the asymmetric N_2O_3 form can be clearly identified: at 244, 411.5, 768.6, 1294, 1625, and 1829 cm^{-1}. The situation with *sym*-N_2O_3 is less clear. The 375 and 1687 cm^{-1} bands clearly refer to this species and possibly also the weak 965 cm^{-1} band. The fractions of the isomers were determined from the temperature dependence of the bands. The difference between the energies of *symm*- and *asymm*-N_2O_3 was calculated: $\Delta H = 1.8 \pm 0.2$ kcal mol^{-1}.

The formation of HBC between benzene and CHF_3 in LKr has also been studied by UV spectroscopy.[62] The measurements were based on the longest-wavelength, the so called ^1L_b band due to the ππ* transition of benzene located in the region of 255 nm. In cryosolutions, the ^1L_b band has fairly pronounced vibronic structure, which makes it possible to study individual vibronic components. For the HBC with benzene, quantitative data have been obtained in the region of the σ_0^1 transition, the band undergoing a hypsochromic shift relative to the band of monomeric benzene on formation of the complex. Heating of the HBC solution in LKr from 120 to 180 K increases the band half-width from 140 to 240 cm^{-1} and decreases the distance between the maxima of the bands of the monomer and the HBC from 240 to 120 cm^{-1}. The enthalpy of complex formation has been determined as 2.0 kcal mol^{-1} from the temperature variation of the equilibrium constant.

VII. NON-LINEAR ABSORPTION OF INFRARED RADIATION AND STIMULATION OF CHEMICAL REACTIONS IN CRYOSOLUTIONS

The influence of vibrational excitation on the reactivity of molecules is nowadays being vigorously investigated. As mentioned in the previous Sections, the use of cryosystems greatly simplifies the form of the spectrum by virtue of the suppression of the hot transitions and the temperature changes are also reduced to a minimum on vibrational excitation as a consequence of the high specific heat of the condensate. The measurement of the populations of various vibrational states is thereby facilitated.

The possibility of carrying out chemical reactions, stimulated by laser radiation, in solutions is of independent interest, since it is possible to establish a higher density of molecules in solution than in the gas phase at the same temperature.

Burtsev and Bulanin[63] investigated the characteristic features of the non-linear absorption of the IR radiation from a CO_2 laser ($\nu = 936.8$ cm^{-1}) in a solution of SF_6 in LKr (at 140 K) in order to estimate the time τ of the V−T relaxation of $\nu_3(SF_6)$ in the cryosystem. Within the framework of the approximations adopted, $\tau = 9$ ns was obtained. In a subsequent study,[64] the same workers used much higher intensities of the laser radiation. An extremely strong saturation of the test solution was observed; for example, at $I_0 = 1.5$ MW cm^{-2}, the transmittance of the specimen increases by a factor of 2×10^3 compared with the transmittance in a weak field. The formalism of the two-level model now no longer ensured a complete agreement with experiment and a model based on a three-level scheme was used to interpret the experimental data. A somewhat shorter vibrational relaxation time of SF_6 was obtained: $\tau \simeq 3$ ns. In the same study, the influence of extraneous substances on the relaxation of SF_6 was investigated. The introduction into the cryosystem of several mole per cent of a molecular admixture has an appreciable influence on the saturation of the absorption, although it does not affect either the position or the width of the SF_6 absorption band. The following relaxation times have been obtained in the presence of additives: 0.15 ns for O_2, 0.06 ns for CH_4, and 0.01 ns for NO. The fast relaxation in the case of NO has been explained by the appearance of low-lying acceptor levels as a result of the dimerisation of NO in the cryosystem.

The SF_6 molecule has also been investigated in liquid O_2 and Ar.[65,66] The V−T relaxation time of SF_6 is ~37 ps in LO_2 and ~160 ps in LAr.

Bertsev and Burtsev[67] chose the ozone molecule as the object of investigation, which is a suitable candidate for carrying out vibrationally-activated reactions in low-temperature condensed

systems. Solutions of O_3 in LAr and LO_2 were investigated at temperatures in the range 90–100 K: τ is ~100 ns in LAr and ~40 ns in LO_2. The result obtained was compared with vibrational relaxation data for O_3 in the gas phase, where the ratio of the efficiencies of Ar and O_2 as deactivators of the (001) state of ozone is known to be ~1:3. The populations of the vibrational states of O_3 were estimated for a specified level of pumping on the assumption that direct V–T relaxation of the (001) level is unlikely and that this state is deactivated stepwise:

$$(001) \xrightarrow{\tau_1} (010);\ (010) \xrightarrow{\tau_2} (000)\ .$$

As a result, it is possible to attain an appreciable population of the excited vibrational level of the O_3 molecules (up to 0.4) and the systems investigated are thus found to be potentially suitable for carrying out reactions involving vibrationally excited molecules in the condensed phase.

In one of the first investigations,[68] a study was made of the relaxation of the vibration of CH_3F in LAr and LO_2 from the saturation of the IR absorption and also experiments were performed on double IR–IR resonance, yielding directly the V–T relaxation time. Thus induced absorption at 1021.2 cm^{-1}, due to the $\nu_3 \rightarrow 2\nu_3$ transition, is observed in the experiment by the double IR resonance method with pumping by radiation at a frequency of 1037.4 cm^{-1}. As for O_3, the CH_3F relaxation time in LAr (1.30 μs) is several times greater than in LO_2 (375 ns) and probability of the V–T transition in the cryosystem is only an order of magnitude higher than in the gas phase for systems of the same type.

Thus the hot transition in the SF_6 spectrum in LKr at 140 K has also been observed by the double IR resonance method.[69] The maximum of this "hot" absorption is displaced by –4.5 cm^{-1} relative to ν_0, the V–T relaxation time of the $\nu_3 = 1$ level is ~3 ns, and the population of this level reaches 0.7. The absorption observed from the excited vibrational level[69] is more suitable for the study of the anharmonic structure of the $\nu_3 \geqslant 2$ states than the diffuse pattern characteristic of the gas phase. The calculation for the transition

$$v_3 = 1\,(F_{1u}) \rightarrow v_3 = 2\,(A_{1g},\ E_g)$$

shows that the anharmonic constants are $X_{33} = -1.2$ cm^{-1}, $G_{33} = 0.53$ cm^{-1}, and $T_{33} = -0.27$ cm^{-1}. According to the authors, the results show that the inversion of the populations does really occur in the optical pumping of cryosystems.

Experiments of another type have been performed with excitation of the N_2 vibrational mode with the aid of an HBr laser. The relaxation of the vibrational energy was followed from the fluorescence of the CO impurity molecule.[65] In the limit reached on decreasing the CO concentration, the relaxation time constant characteristic of pure LN_2 was obtained: ~0.018 s^{-1}. Overall, the rates of collision-induced vibrational deactivation in liquid CO–N_2 mixtures are low and the radiation-induced decomposition processes predominate as vibrational energy is lost in solution. The principal result of these measurements is that, at least for the system investigated, the kinetics of the vibrational exchange in simple cryogenic liquids do not differ greatly from those in a dilute gas; the rate constants measured in the gas phase can be simply extrapolated to the density of the liquid phase without any significant correction. Lupo et al.[70] reached an analogous conclusion having measured the rate constant for energy transfer from CO to O_2 in LAr in the temperature range 86–145 K:

$$CO(v=1) + O_2 \rightarrow CO + O_2(v=1) + \Delta E,$$

where $\Delta E = 589$ cm^{-1}. The rate constant for the quenching of the CO fluorescence in the above temperature range is higher by a factor of ~3 but remains equal to values for the gas phase within the limits of experimental error. The vibrational relaxation of CO in the presence of CH_4, CD_4, and CF_4 is several times faster than both for the solution in LAr and for the gas phase.[71] In the absence of impurities, the V–T relaxation in the CO solution in LAr is not the dominant process, the purely radiation-induced relaxation with a lifetime of 18 ns predominating.[72] With increase in CO concentration, the radiation was reabsorbed and the lifetime increased to 1 s. Isotope-enriched carbon monoxide (88% $^{13}C^{16}O$, 12% $^{13}C^{18}O$) in LAr has been optically pumped to the $v = 1$ level by means of a continuous CO laser.[73] As a result of the collision-induced redistribution of energy, some of the molecules were excited to higher vibrational states; fluorescence was recorded from vibrational levels up to $v = 20$ and the inversion of the populations of the level was noted.

A transition from an excited vibrational state to an excited electronic state is not ruled out either. When matrix-isolated $^{13}C^{18}O$ in Ar was irradiated by a colour-centre laser, the frequency of the radiation of which coincided with the first overtone of the CO band, fluorescence was observed in the visible and UV part of the spectrum.[74]

Overall, by virtue of the relatively slow V–T relaxation in solutions in liquefied monatomic gases, a high population (tens %) of the excited vibrational states of the impurity diatomic molecules in cryosolutions is readily attained. However, it seems unlikely that multiphoton IR excitation should occur in polyatomic molecules dissolved in cryogenic liquids. SF_6 dissolved in LAr, LO_2, and LN_2 has been irradiated[66] by a CO laser using a power much greater than that employed in multiphoton experiments in the gas phase, but no traces of dissociation were observed.

Processes in which single-photon IR excitation can increase the rate of reaction between an excited molecule and other molecules in the cryogenic solution are of interest. Such a process has apparently been discovered. The reactions of ozone with NO in the cryosystem stimulated by IR radiation have been investigated.[75] Preliminary experiments showed that the solutions of O_3 in NO at temperatures in the range 130–160 K are fairly stable. The character of the spectrum shows that the formation of a complex between NO and O_2 cannot be ruled out.

When the solution is irradiated by a CO_2 laser ($\lambda = 9.5$ μm), the concentration of excited O_3 molecules is about 10%. It was established that the irradiation leads to a rapid loss of O_3 from the solution: after 20 pulses, the O_3 concentration decreased by 30–50%, which corresponds to a quantum yield of the order of 3×10^{-2} molecules per photon under the experimental conditions. This result demonstrates the real occurrence of the stimulation of a reaction in cryosystems by IR radiation.

In a two-step IR–UV isotope separation process, an IR photon can be used to excite selectively the vibrational state of one of the isotope-substituted derivatives, while a UV photon can lead to the dissociation of vibrationally excited molecules. The possibility of marking molecules with the aid of an IR photon and then of the excitation of only the marked molecules by another photon has been demonstrated in measurements of double IR–IR resonance (see above).[65,69]

VIII. PHOTOCHEMICAL REACTIONS IN CRYOSOLUTIONS

The transparency of cryosolvents in the UV region facilitates photophysical studies and the weak interaction of the molecules with the solvent makes it possible to investigate molecules virtually in a free state. On exposure to a picosecond pulse (λ = 505 nm), predissociation of I_2 in LXe ($\tau \simeq 14$ ps) and the subsequent primary recombination ($\tau \simeq 40$ ps) were observed.[22] As a result of the photoexcitation of HCl in LXe (λ = 193 nm), IR fluorescence of HCl from the $v = 1$ state was noted.[76] The formation of vibrationally excited HCl molecules as a result of triple collisions of H and Cl atoms with Xe is the most probable. Emission by HCl from the $v = 2$ level appears[77] in SXe and the rate of relaxation from the $v = 1$ level diminishes. Both these effects have been attributed to the loss of mobility by HCl in the solid phase and the consequent decrease in the intensity of the interactions between the HCl molecules. It has also been shown[78] that the rate constant for the deactivation of DCl is smaller than that for HCl. It has been suggested that the rotational degrees of freedom also play a role in the vibrational relaxation of molecules in the liquid phase.

Photochemical reactions have been studied systematically by Turner and Poliakoff[2] using cryostats described previously.[9,13] Oskam's group[79,80] has been working on the same lines. The interaction of the environment in a solid matrix with the complex $Cr(CO)_5$ obtained on UV photolysis of $Cr(CO)_6$ had been investigated earlier from the position of the absorption band of the pentacarbonyl complex in the visible part of the spectrum.[81] For a series of matrices (CH_4, Xe, Kr, Ar, CF_4, SF_6, and Ne), the absorption band shifts from 480 to 640 nm. The magnitude of the shift shows that no solvent is completely inert towards $Cr(CO)_5$ and that the influence of trace impurities may be important in photochemistry.[82]

The first experiments in cryogenic solutions were performed in order to obtain complexes of metal carbonyls with N_2.[83] A band at 2236 cm^{-1}, associated with the $\nu(N-N)$ vibration, has been clearly observed in the IR spectrum of $Cr(CO)_5N_2$. A careful study[84] demonstrated that more prolonged photolysis of $Cr(CO)_6$ in LXe at a higher N_2 concentration makes it possible to obtain species with a higher N_2 content. Narrow-band photolysis at 367 nm in a solution in LXe containing N_2-substituted $Cr(CO)_{6-x}(N_2)_x$ complexes decomposes certain compounds while leaving others comparatively unaltered. At the same wavelength (corresponding to $d-d$ transitions), different isomers have markedly different absorption intensities and respond differently to irradiation. Thus the *cis*- and *trans*-isomers of $Cr(CO)_4N_2$ and the *mer*- and *fac*-isomers of $Cr(CO)_3(N_2)_3$ have been clearly separated. The introduction of additional N_2 molecules reduces the thermal stability of the complexes; it has not been possible to identify the $Cr(N_2)_6$ complex at −79 °C in solution in LXe.

Using a cell with four windows, Maier et al.[85] were able to obtain the IR spectra of the very unstable compound $Ni(CO)_3N_2$ as a result of the photolysis (λ = 286 nm) of $Ni(CO)_4$ in LKr with added N_2 at −170 °C. On switching off the UV lamp, the IR spectrum of Ni.$(CO)_3N_2$ (2267.5, 2101.0, and 2030.0 cm^{-1}) disappears fairly slowly and the kinetic parameters of the reaction

$$Ni(CO)_3N_2 + CO \rightarrow Ni(CO)_4 + N_2$$

were measured. The disappearance of the $Ni(CO)_3N_2$ bands follows first order kinetics. However, the kinetics are complicated by the dependence of the reaction rate constant both on the CO concentration and on the N_2/CO ratio. This agrees with the hypothesis of the occurrence of two competing processes in the reaction. One is dissociative in character, while the other results in CO participating in the transition state.[86]

The possibilities in the study of the kinetics of ligand substitution in liquefied gases can be seen particularly clearly in relation to the reaction of the complex $Fe(CO)_2(NO)_2$ with N_2 in LKr.[87] After UV photolysis for 4 min, the intensity of the bands due to $Fe(CO)_2(NO)_2$ fell and bands appeared at 2257.5 cm^{-1} [$\nu(N-N)$], 2046.0 cm^{-1} [$\nu(CO)$], and 1805.1 and 1761.5 cm^{-1} [$\nu(NO)$]. After further photolysis, additional bands appear at 2250.5 and 2228.0 cm^{-1} [$\nu(N-N)$] and 1796.3 and 1749.4 cm^{-1} [$\nu(N-O)$]. The experiments described indicate the stepwise substitution of CO by N_2. The primary photoproduct $Fe(N_2)(CO)(NO)_2$ is stable at −155 °C and begins to vanish only after the solution has been heated to −107 °C. Thus, in addition to the information obtained in matrix isolation experiments about the existence of complexes, in cryosolutions it is possible to obtain data concerning their stability and hence also their thermodynamic parameters.

The photolysis of $Cr(CO)_6$ in pure LXe or LKr with 5% of added LXe gives rise to the IR bands of an intermediate compound ($\tau_{1/2} \simeq 2$ s at −98 °C), which may be due to the unstable complex $Cr(CO)_5$...Xe.[88] In the absence of Xe, these bands were not observed in the spectrum.

The simplest complex of H_2 with a d^6 metal is $Cr(CO)_5H_2$. Its existence as a reaction intermediate has been postulated and it has been the object of several theoretical studies. UV photolysis of $Cr(CO)_6$ dissolved in LXe with added H_2 [89] leads to the formation of a new carbonyl-containing compound, which was not observed in the absence of H_2. The spectrum of the compound has a broad absorption in the near UV region at 370 nm and the compound is decomposed by the UV light at this wavelength:

$$Cr(CO)_6 + H_2 \underset{367\ nm}{\overset{228\ nm}{\rightleftarrows}} Cr(CO)_5(H_2) + CO\,.$$

The IR spectrum of the compound in the region of the CO vibrations has three bands: at 2094, 1974.3, and 1971.9 cm^{-1}. When D_2 is introduced into the complex, the low-frequency band undergoes a distinct downward shift by ~ 1 cm^{-1}. The shift is not caused by a solvent effect, which led the authors to the conclusion that they had obtained a hydrogen-containing compound. The three $\nu(VO)$ bands agree with the C_{4v} symmetry of the $Cr(CO)_5$ ($2a_1 + e$) fragment. This structure was confirmed by the preparation of a hydrogen-containing complex from $Cr(^{12}CO)_5(^{13}CO)$; as expected, the decrease in symmetry leads to the appearance of additional CO bands. A comparatively broad band with a maximum of 3030 cm^{-1}, which shifts to 2241 cm^{-1} for the deuterio-derivative, was also observed in the spectrum. The shift is somewhat smaller than for the isolated H_2 molecule, but the authors believe that an interaction with the CO vibrations must be considered. These bands have been assigned unambiguously[89] to the H−H and D−D stretching vibrations of the molecular hydrogen in the complex, which proved to be entirely stable up to −35 °C even after the evacuation of a large part of the excess H_2.

A comparative study has been made[90] of the interaction of the complexes $M(CO)_6$ (M = Cr, Mo, or W) with H_2 in LXe: $M(CO)_5$.(H_2) is always formed and in the case of Cr and W *cis*-$M(CO)_4(H_2)_2$ is also produced. The complex $W(CO)_5(H_2)$ has likewise been obtained in solution in LXe.[91] The $\nu(H-H)$ frequency for the Cr complex quoted above (3030 cm^{-1}) proved to be intermediate between the values for the molybdenum (3080 cm^{-1}) and tungsten (2711 cm^{-1}) complexes. The stability of the chromium complex in

LXe is greater than that of the molybdenum complex and smaller than that of the tungsten complex. Under D_2 pressure, the exchange reaction

$$Cr(CO)_5(H_2) \rightarrow Cr(CO)_5(D_2)$$

takes place. HD is probably formed as a result of the intramolecular exchange

$$Cr(CO)_5(H_2)(D_2) \rightarrow Cr(CO)_4(HD)_2 .$$

Metals with the d^8 configuration form dihydrides and not complexes with H_2. UV photolysis of $Ru(CO)_4PPh_3$ and H_2 dissolved in supercritical Xe at room temperature leads to the formation of $Ru(CO)_3(H_2).PPh_3$—an unstable dihydride, the existence of which in heptane at higher temperatures and an H_2 pressure of 550 atm had been reported earlier. The 1892.3 and 1810 cm^{-1} bands, which are more distinct in LXe than in heptane, were assigned to Ru—H bond vibrations.

The interaction, on photolysis, of H_2 with the most active catalysts for homogeneous catalysis, namely $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ in LXe at −104 °C and under a 10—20 atm H_2 or D_2 pressure, had also been investigated.[92] The coordinated H_2 or D_2 molecules in $Fe(CO)(NO)_2(H_2)$ and $Co(CO)_2(NO)(H_2)$ were identified from the IR bands at 2973 and 2195 cm^{-1} and 3000 and 2228 cm^{-1} respectively. The symmetrical and antisymmetric stretching vibrations of the $M-H_2(D_2)$ were also assigned. Experiments in LXe showed that the reaction proceeds via the same pathways as in the usual solvent but at the same time it is possible to follow them in greater detail. It was found that the complexes of molecular H_2 are more abundant than had been supposed and that hydrogenation reactions, especially photocatalytic reactions with metal carbonyls, can proceed via the coordinated H_2 and not via metal hydrides.

Previously unknown complexes of ethylene with $Cr(CO)_6$ derivatives, namely $Cr(CO)_5(C_2H_4)(m)$, $Cr(CO)_4(trans\text{-}C_2H_4)_2(t)$, and $Cr(CO)_4(cis\text{-}C_4H_4)_2(c)$, have also been obtained on LXe at −78 °C.[93]

Brief photolysis at very low C_2H_4 concentrations yielded the complex (*m*) (with the IR bands of the CO groups at 2078.9, 1967.4, and 1960 cm^{-1}). At a higher C_2H_4 concentration, the complexes (*c*) (2036.8, 1949.3, and 1913 cm^{-1}) and (*t*) (1953.1 cm^{-1}) were formed. Bands referring to the C_2H_4 vibrations also appear in the IR spectrum in the range 1000—1600 cm^{-1}. The structures of the complexes were established spectroscopically: C_{2v} for (*m*), C_{2v} for (*c*), and pseudo-D_{4h} for (*t*).

Similar experiments with $Mo(CO)_6$ and $W(CO)_6$ lead to the formation of not only the previously known complexes (*m*) and (*c*) but also of the unknown analogues (*t*) for Mo and W. In contrast to the unstable chromium complexes, the molybdenum and tungsten complexes are stable under the experimental conditions.

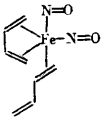
When the photolysis of $Co(CO)_3$ was carried out in LXe with added but-1-ene, it was clear from the spectrum that the photoproduct contains two CO groups and one NO group. The fourth coordination site is apparently occupied by the π-linked olefin.[2]

The photolysis of the $Fe(CO)_2(NO)_2$—but-1-ene system in LXe proceeds with formation of two photoproducts:[94]

$$Fe(CO)_2(NO)_2 \xrightarrow{h\nu} Fe(CO)(NO)_2(\eta^2\text{-}1\text{-}C_4H_8) \xrightarrow{h\nu} Fe(NO)_2(\eta^2\text{-}1\text{-}C_4H_8)_2 .$$

No signs of the decomposition of either complex in LXe were observed for 1 h at −104 °C.

A greater variety of products is attained in the reactions of the same complexes $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ with buta-1,3-diene in LXe, since the η^2-C_4H_6 and η^4-C_4H_6 derivatives are obtained.[95] Under similar photolytic conditions in LKr, $Ni(CO)_4$ affords only $Ni(CO)_3(\eta^2\text{-}C_4H_6)$, which is thermally less stable than the above iron and cobalt complexes. The compound $Fe(CO)_2(NO)_2$ forms a bis-η^2-butadiene complex, which can be regarded as an active intermediate in dimerisation reactions. The catalytic process apparently proceeds via a pentacoordinate intermediate with a bent NO group:



This intermediate, which has three coordinated C=C bonds, leads to the formation of mainly 4-vinylcyclohexene and not other possible dimers such as cyclo-octadiene. The stabilising role of the hydrocarbon ligand has been discovered in the photochemical synthesis of $(\eta^4\text{-}C_4H_6)Fe(CO)_2(N_2)$ in solution in LXe with added 1.7% N_2 at −110 °C.[96] No decomposition of the complex was observed on heating the solution to −80 °C.

The photolysis of $CpRh(C_2H_4)_2$ dissolved in LXe with added N_2 at 173 K leads to the splitting off of C_2H_4 and the formation of $CPRh(C_2H_4)(N_2)$.[97]

The experiments described here show that LXe is a solvent which yields additional information compared with low-temperature solid matrices and solutions at room temperature.

Naturally, the photochemical processes in the cryosolutions are not restricted to organoelemental compounds. It has been demonstrated for formaldehyde[23] that it is possible to carry out even isotopically selective processes (see Section V). When a mixed solution of CD_2O and CH_2O in LXe is irradiated, the concentration of each component decreases linearly with time, which indicates cross-order kinetics. the CD_2O concentration then falls somewhat faster than that of CH_2O; this is clearly indicated by the relative intensities of the IR bands of CD_2O and CH_2O. At −94 °C and −106 °C and at irradiation wavelengths of 325 and 318.7 nm, the preferential decomposition of CD_2O (by a factor up to two) was attained. The quantum efficiency of the photo-decomposition of CH_2O at 325 nm is ~0.001. The ratio of the rates of decomposition of the CD_2O and CH_2O molecules is approximately proportional to the ratio of the optical densities in their spectra at the excitation wavelength.

The dissociation of molecules in solution in simple gases has also been achieved using the UV radiation generated by the electrical breakdown of the liquid medium effected by an intense CO_2 laser:[65]

$$OCS + h\nu \rightarrow CO + S;\ C_2H_4 + h\nu \rightarrow C_2H_2 + H_2;\ O_2 + h\nu \rightarrow 2O(^3P) .$$

The construction of lasers with a tunable frequency combined with the characteristics of the cryosolutions should lead to further development of photocheistry in the condensed phase. On the other hand, in order to investigate the reaction mechanism, it is useful to apply the methods of the high-speed IR spectroscopy developing at the present time.[2,98-100] With the aid of multichannel Raman spectrometers, it is possible to record rapid processes up to the picosecond range. In experiments with solvents such as N_2, O_2, and Ar,[101] it was found that the low solubilities make the Raman method rather unpromising. However, the comparatively high solubilities of the molecules in LXe give rise to the hope that Raman

spectroscopy will find extensive application in the study of the mechanisms of photochemical reactions.

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Thus reactivity and chemical reaction mechanisms can be studied spectroscopically in solutions in liquefied elemental gases. The low temperatures and the weak interaction of the molecules with the solvents make it possible to obtain the spectra of reactive and unstable compounds with standard instruments. The absence of absorption by the solvents at wavelengths ranging from UV to far infrared ensures the possibility of investigating the effect of laser radiation on the course of reactions. The measurement of the spectra of very thick layers of solution (up to several metres) compensates for the relatively low solubility of molecules and renders the method general.

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Photoelectron Spectroscopy of Organofluorine Compounds

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The analysis of the photoelectron spectra of organofluorine compounds is described. The influence of substitution by fluorine on the electronic structure of the molecules is examined on the basis of experimental data and quantum-chemical calculations. A table of the ionisation energies of organofluorine compounds is presented.
The bibliography includes 170 references.

CONTENTS

I. Introduction 745
II. Fluorine-containing alkanes and halogenoalkanes 745
III. Fluorine-containing alkenes and halogenoalkenes 748
IV. Fluorine-containing alkynes and halogenoalkynes 749
V. Fluorinated aromatic compounds 750
VI. Fluorinated organic compounds containing nitrogen, oxygen, and sulphur atoms 751

I. INTRODUCTION

The wide-scale application of organofluorine compounds in various branches of science and engineering is responsible for the great interest by chemists in the study of their electronic structure and reactivity. The commonest method of securing information about electronic structure is nowadays the photoelectron spectroscopy of molecules (PES),[1-4] which permits a direct comparison with experiment of various quantum-chemical models used for the calculation of the physicochemical characteristics of molecules.

The aim of the present review is the analysis of data obtained for organofluorine compounds by the PES method. Although there are several reviews of a general character (see, for example, Vovna and Vilesov[2] and Rao et al.[5]) as well as reviews for individual classes of compounds,[6,7] data on organofluorine compounds have not been described systematically or discussed. One may mention only two communications[8,9] in which photoelectron spectra (PE spectra) are presented without discussion for a series of fluorine-containing compounds together with tables of experimental and calculated ionisation energies. This review discusses the results of the most detailed investigations, which are naturally available only for not unduly complex molecules. Examples of the application of PES to the study of the correlation between the electronic structure of fluorine-containing molecules and their reactivity are examined. In order to cover fully the studies on the PES of organofluorine molecules, the review presents a table of the first ionisation energies of the molecules of compounds in all the classes considered.

The information which can be extracted from the PES refers strictly speaking not to the neutral molecule but to the corresponding molecular radical-cation, PES yielding the spectrum of the energy states of the molecular ion. However, the PE spectra are frequently interpreted using the Koopmans theorem by comparing the PE spectral bands with a definite molecular orbital (MO) of the ground electronic state of the neutral molecule. In this approximation, PES yields the binding energies of the electrons in different MO (ionisation energies) and the band shape is determined by the character of the localisation of the electron in the corresponding MO (distribution of electron density).

The relation between the ionisation energy (EI) and the orbital energy (ε_ρ) is expressed by the equation

$$IE - (-\epsilon_\rho) = \Delta E_{cor} + \Delta E_{reorg},$$

where ΔE_{cor} is the difference between the correlation energy of the ion and the molecule ($\Delta E_{cor} > 0$) and ΔE_{reorg} is the reorganisation energy ($\Delta E_{reorg} < 0$).[2] For the Koopmans theorem to be valid, the equality $\Delta E_{cor} = -\Delta E_{reorg}$ must hold. A detailed analysis of the Koopmans theorem may be found in two monographs.[2,4] Both non-empirical and semiempirical quantum-chemical calculations, carried out using the Koopmans theorem, sometimes fail to yield a satisfactory agreement with experimental EI. Despite this, the MO concept remains fairly fruitful both in the analysis of the PE spectra and in the study of the reaction mechanisms and of the structure of organic compounds.[10]

The concept of the weighted mean (with respect to the degree of degeneracy of the MO) ionisation energy of the unshared (lone) electron pair of the halogen atoms has been introduced[1] and linear correlations have been established between the ionisation energies and the valence and inner electrons of the halogens, which it has been suggested can be used for the identification of the lone electron pair bands in the PE spectra. The authors of the above study note that, in establishing correlations for fluorine-containing compounds, definite difficulties arise associated with the necessity to re-examine the existing interpretation of a number of spectra in the literature. Apparently, as a result of the marked delocalisation of the unshared (lone) electron pairs (LEP) of the fluorine atom, the proposed correlations must be used with much caution.

II. FLUORINE-CONTAINING ALKANES AND HALOGENOALKANES

Fluorinated halogenomethanes are the most thoroughly investigated compounds of this class.[12-17] The most thorough experimental study of CH_nF_{4-n} is one[17] in which the PE spectra were obtained by excitation with the HeI and HeII lines, the vibrational structure was analysed, a comparison was made with the absorption spectra and photoionisation mass-spectrometric data, and calculations of the

electronic structure were carried out in terms of the Hartree–Fock approximation. The above investigation included also the analysis of the theoretical and experimental data obtained previously.

The substitution of a hydrogen atom by a fluorine atom greatly complicates the PE spectra both as a result of the increase in the number of valence electrons and owing to the decrease in symmetry. Even in the PE spectrum of CH_3F the second band consists of a superposition of two unresolved bands. X-Ray electronic spectra have been obtained[18] in the valence region and the complex bands with Lorentzian profile were resolved using the calculated intensities of the individual bands. The vertical ionisation energies (EI) obtained are used in comparing theory and experiment. Here it is necessary to bear in mind that, owing to the large step (0.16 eV) in the measurement of the PE spectra and the low resolution, the accuracy of the determination of the EI is low and probably does not exceed a level to within 0.2 eV.

Despite the difficulties mentioned, the interpretation of the PE spectra of fluoromethanes can be regarded as fairly reliable. The sequence of the MO for these molecules in order of increasing ionisation energy is presented in Fig.1. Some uncertainty remains in the sequences of the close MO $1b_1$, $3a_1$, and $2b_2$ for CH_2F_2 (in the EI range 18.5–19.8 eV). We present the sequence proposed[19] on the basis of calculations in terms of the $X\alpha$ approximation with overlapping spheres. Another sequence has been obtained for this energy range in other studies.[9,17,18]

The nature of the majority of the MO in CH_nF_{4-n} is complex because of the pronounced mixing of the atomic orbitals of fluorine with the σ orbitals of carbon. On the basis of the results of Du Li et al.,[19] only the MO $3b_2$ and $1a_2$ (EI = 15.2 and 15.6 eV) in CH_2F_2 can be regarded as localised on the fluorine atoms. According to Brundle et al.,[17] the MO $4e$ with EI = 17.2 eV in CF_3H and $1e$ with EI = 18.5 eV in CF_4 are closest to the unshared electron pair of fluorine, while in CH_3F the unshared electron pairs of fluorine do not exist in a pure form. One should note that different methods of calculation yield appreciably different results for the MO populations.[17,19–21] However, the band widths in the PE spectra agree with an appreciable delocalisation of the unshared electron pairs of fluorine.

The character of the highest occupied MO (HOMO) is especially important in the study of reactivity. For all the fluorine-substituted methanes except CF_4, the HOMO is bonding in relation to the C–H bond and antibonding in relation to the C–F bond.[17] In CF_4, the HOMO of the C–F bond must be bonding, since the removal of an electron from this MO is accompanied by the dissociation of the molecular ion.[22]

The PE spectra of C_2H_5F and n-C_3H_7F have been published.[9,23–25] It is seen from these data that the HOMO of the C–C bond in the alkyl fluoride is bonding. The first vertical EI decrease with increase in the length of the alkyl chain but remain approximately 0.4 eV higher than the EI of the corresponding alkanes owing to the high electronegativity of the F atom. The same effect leads to a further increase in EI with increase in the number of F atoms in $C_2H_nF_{6-n}$.[25] However, the spectra become so much more complex that even for $n = 2$ it is possible to distinguish only three bands.

The introduction of a single halogen atom X (X = Cl, Br, or I) into perfluoromethane lowers the molecular symmetry to C_{3v} and leads to the partial removal of the degeneracy of the MO (Fig.2). In the low-energy part of the PE spectrum, the bands of the unshared electron pairs of the X atom, corresponding to the removal of the electron from the HOMO, can be readily differentiated both as regards shape and the characteristic spin–orbital splitting. The first vertical EI decrease appreciably in the sequence Cl, Br, I (13.08, 12.12, and 10.45 eV). The bands of the n_X electrons are followed by the band of the C–X bonding MO with vertical EI of 15.20,

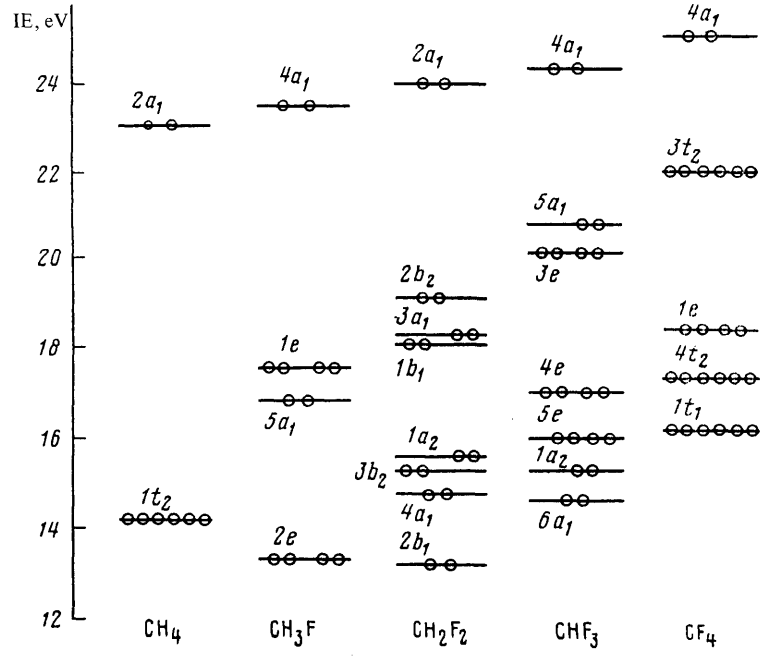


Figure 1. Schematic arrangement of the molecular orbitals of CH_nF_{4-n}.

14.28, and 11.18 eV for Cl, Br, and I respectively. In the region of higher energies, the PE spectra of all three halogenotrifluoromethanes are similar,[14,15,26-29] Despite the large number of bands, one can resolve all the bands whose appearance is possible up to an energy of 24 eV. Analysis of the vibrational structure, the change in band intensity on passing from excitation by the HeI line to excitation by the HeII lines, and comparison with the CF_4 and CF_3H spectra made it possible to interpret all the bands unambiguously.[15,16] The following sequence of MO was obtained: $1a_1$(C2*s*); $1e$(CF_3); mixed orbitals of the unshared electron pairs of the F atom and the C–F bond; $2a_1$, $2e$, and $3e$; $1a_2$(F); $3a_1$(C–X); $4e$(X). Calculations by the extended Hückel (EHM) and CNDO/2 methods for CF_3Cl and CF_3Br yield the reverse sequence of the MO $1a_2$ and $3e$.[20]

An increase in the number of isotypical X atoms in $CF_{4-n}X_n$ leads to a further decrease in EI and to a redistribution of the band intensity in the PE spectra between the high-energy and low-energy parts, since the EI of other halogens are lower than the EI of fluorine. For X = Cl or Br and n = 1–3, it has been possible to differentiate and identify virtually all the stretching vibration bands of the electrons.[13-16,27,28] The following sequence of MO was obtained: $3b_2$, $3b_1$, $2a_2$, $4a_1$, $2b_2$, $2b_1$, $1a_2$, $3a_1$, $1b_1$, $2a_1$, $1b_2$, and $1a_1$ for CF_2X_2 and $1a_1$, $4e$, $3e$, $3a_1$, $2e$, $1e$, $2a_1$, and $1a_1$ for CFX_3. The four highest MO are those of the unshared electron pairs of the atom X. The $(4e)^{-1}$ and $(3e)^{-1}$ bands in PE spectrum of $CFBr_3$ exhibit spin–orbital splitting. The sequence of the MO of the unshared electron pairs of the atoms X in CF_2X_2 and CFX_3 differs from the sequence of the MO of the corresponding X-substituted derivatives of methane not containing fluorine.[12,19,30,31] If the increase in EI on passing from perfluorinated halogenomethanes to the fluorinated derivatives is attributed to the inductive influence of the fluorine atom, then the inductive effect is found to be different for different MO.

The PE spectra of a series of less symmetrical fluorine-containing halogenomethanes have been obtained and interpreted in fair detail: $CHFCl_2$, CHF_2Cl, CH_2FCl, and CF_2BrCl.[12-14,26,28] The HOMO are described satisfactorily by the AO of the unshared electron pair of the Cl atom for the first three molecules and the AO of the Br atom for the last. The most thorough studies of both fluorinated and fluorine-free halogenomethanes have been carried out by a group of Yugoslav spectroscopists,[12-16] who paid special attention to the influence of the changes in the energy of ionising radiation (the HeI and HeII lines) on the spectra. They established that the sensitivity of the bands with an appreciable contribution by the unshared electron pairs of the halogens decreases in the sequence F ≫ Br ≅ I > Cl. This regularity can be usefully borne in mind in differentiating the bands corresponding to the removal of electrons from different halogen atoms.

Successive fluorination of ethane leads to the stabilisation of the HOMO, which is C–C bonding in character.[9,23,25] A fairly complete analysis of the PE spectrum has been carried out only for C_2H_5F.[9] Semiempirical calculations of the electronic structure yielded the following MO sequence: $3a''$(CH), $10a'$(Cl), $9a'$(C–H), $2a''$(F), $8a'$(C–F), $1a''$(F, C–H), $7a'$(F), $6a'$, and $5a'$.[41] However,

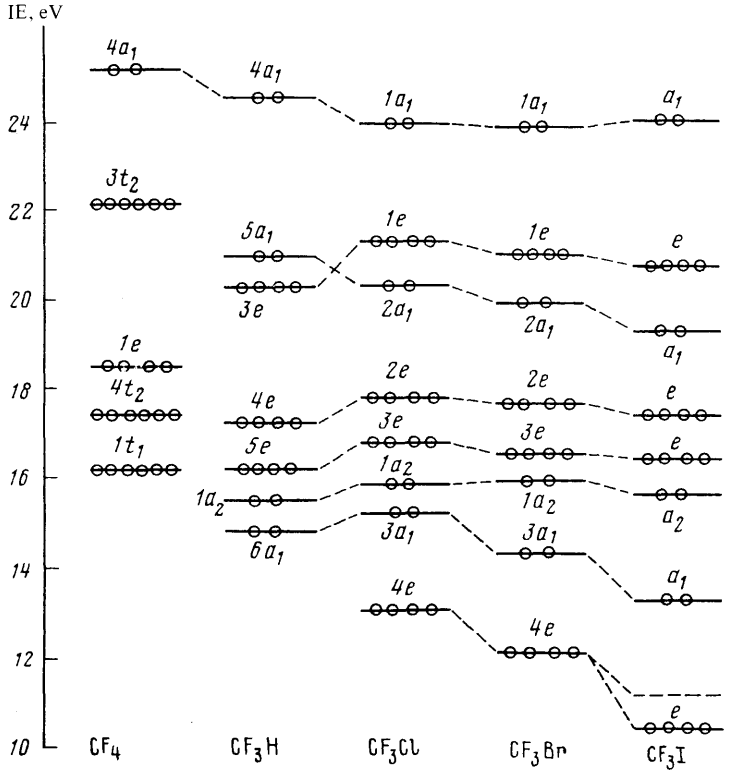


Figure 2. Schematic arrangement of the molecular orbitals of trifluoromethanes CF_3X, where X = H, F, Cl, Br, or I.

the observed regularities in the variation of the first EI in the successive fluorination of methane and ethane agree better if the highest two occupied MO are interchanged.

The introduction of Cl, Br, and I atoms into fully or partly fluorinated ethane entails the same changes in the PE spectrum[26,32-34] as those examined above for methane. The spectra of $(CF_2X)_2$, where X = Cl, Br, or I, have been analysed in greatest detail,[32] but in this case too the number of bands identified is appreciably smaller than expected even when account is taken of only the valence *p* electrons of the atoms.

Analysis of the spectra of halogenoethanes is complicated by the fact that the specimens consist of mixtures of *gauche*- and *trans*-isomers. A structure attributed to the ionisation of individual isomers was discovered only for $(CF_2I)_2$ [32] and CH_2FCH_2Br [33] in the region of the spectra corresponding to the removal of one of the electrons of the unshared electron pairs of I and Br. For $(CF_2I)_2$, EI proved to be higher by 0.1 eV for the *gauche*-isomer, while for CH_2FCH_2Br it proved to be higher by 0.2 eV for the *trans*-isomer. Higher values of the EI for the *anti*-isomers have been obtained also for a series of monofluoro- and monobromo-derivatives of propane and butane and also for *trans*-1-bromo-2-fluorocyclohexane.[33] The bands have been assigned to different conformers[32,33] on the basis of semiempirical calculation. Gounelle et al.[33] took into account only the interaction through space, while Chan and McDowell took into account[32] also the interaction through σ bonds. Possibly the different sequences of the EI of the conformers of derivatives of ethane obtained in these two studies may be associated with this factor.

III. FLUORINE-CONTAINING ALKENES AND HALOGENOALKENES

All the studies on fluorine-containing molecules with an isolated double bond carried out by the PES method concern ethylene derivatives $R^1R^2CCR^3R^4$ (R^1, R^2, R^3, R^4 = H, F, or CF_3). The first EI correspond to the removal of the π electrons of the double bond.

For all the six fluorinated ethylenes,[35-38] the PE spectra were obtained with excitation by the HeI and HeII lines, the variation of the parameter of the angular anisotropy of the scatter of the photoelectrons has been studied for all the spectral bands in the region up to 20 eV, the vibrational band structure has been analysed,[36,38] and empirical and non-empirical calculations, including many-particle calculations, of the electronic structure have been performed.[35,39] This made it possible to interpret fairly reliably the spectra in the region up to 25 eV taking into account all the valence electrons, although some of the ionisation transitions then proved to be somewhat degenerate with respect to energy.

Successive fluorination of ethylene hardly alters the HOMO energies (the vertical EI are in the range 10.38 – 10.69 eV). Such behaviour can be explained by the compensation of the inductive influence of the F atoms and by the interaction through space between the π MO of the C=C bond and the AO of the unshared electron pairs of fluorine ($n-\pi$ conjugation). Indeed, both quantum-chemical calculations[35] and the observed variation of the parameter of angular anisotropy[36] for the series of fluorethylenes indicate an appreciable contribution by the AO of fluorine to the HOMO. The second EI, corresponding to the removal of σ electrons, increase appreciably with increase in the number of F atoms in the substituted ethylene; for example, the second EI of perfluoroethylene is higher by 3 eV than that of the unsubstituted ethylene. The different influences of the substitution of hydrogen by fluorine on the energies of the π and σ MO have been called the perfluoro-effect, the fluorination of ethylene being regarded as the classical example of the manifestation of the perfluoro-effect in planar molecules.[3,4,38] However, more thorough experimental theoretical study[35,39] showed that the shifts of both σ and π MO depend greatly on the nature of the MO and can vary within wide limits (see below). The almost complete agreement between the PE spectra of *cis*- and *trans*-1,2-difluoroethylenes, which agrees well with the many-particle calculations for these molecules, is noteworthy.[35] Semiempirical calculations in terms of the CNDO approximation yield appreciably different MO schemes for the isomers.

Complete fluorination of propene, *cis*- and *trans*-but-2-enes, and 2,3-dimethylbut-2-ene increases the first vertical EI by 1.3 – 4.0 eV.[40-43] However, the variation of the EI with *n* in $C_2H_{4-n}(CF_3)_n$ is irregular and its explanation requires further experimental and especially theoretical studies of the electronic structure. Among other fluoropropene derivatives, only 3-fluoropropene has been studied in fair detail, although a complete interpretation of the spectrum has not been carried out.[44-46] The regularities in the variation of the first ionisation potential in the C_3H_5X series, where X = F, Cl, Br, or I, have been considered as the first semiquantitative demonstration of the existence of "hyperconjugation".[46]

Scott and Russell[47] carried out a joint empirical analysis of the PE spectra and UV absorption spectra of chlorofluoroethylenes. With the aid of the experimental quantities obtained, characterising the successive substitution of hydrogen atoms by fluorine or chlorine atoms, they were able to reproduce the experimental energies of the highest occupied and lowest unoccupied MO of nine chlorofluoroethylenes.[48,49] The introduction of chlorine or bromine atoms into fluorinated ethylenes (the spectra of fluoroiodoethylenes were not obtained) leads to an appreciable (by 0.3 – 1.0 eV) decrease in the first EI corresponding to the removal of π electrons[43,47,49] owing to the effect of $n-\pi$ conjugation. Detailed quantitative studies of this effect for the compounds considered are not described.

A second characteristic feature of fluorohalogenoethylenes is the presence in the PE spectra of the bands due to the LEP of the chlorine and bromine atoms and the bands associated with the C – X bonds. They appear in the energy range (11 – 15 eV) which in the spectra of fluoroethylenes is free from bands and can be readily identified from their characteristic features (see above).

The electronic structure of allene is characterised by the presence of two systems with mutually perpendicular nodal planes. The corresponding MO are degenerate in both allene and perfluoroallene and are HOMO.[50,51] In contrast to fluorinated ethylenes, an appreciable increase (by 1.3 eV) in the first EI is observed, which the authors[51] explained by the predominance of the effect due to negative hyperconjugation and of the inductive effect over $n-\pi$ conjugation.

In 1,1-difluoroallene, the degeneracy of the π MO is removed, since $n-\pi$ conjugation is ruled out for symmetry reasons in the case of the π MO localised on the C(2)=C(3) bond and hyperconjugation is ruled out for the π MO of the C(1)=C(2) bond.[51] As a result, the HOMO is the bonding π MO of the C(1)=C(2) bond. The second π MO of the C(2)=C(3) bond lies 1.5 eV lower. The nonequivalence of the two π bonds in 1,1-difluoroallene [the C(1)=C(2) bond is characterised by an excess electron density, while the C(2)=C(3) bond is characterised by its electron deficiency compared with the bonds in allene and perfluoroallene] is manifested in the chemical reactions of 1,1-difluoroallene.

In tetraflurobutatriene, all the fluorine atoms are located in the nodal plane of the highest occupied π MO of the C(2)=C(3) bond, whose energy (9.3 eV) has not changed compared with butatriene

(the perfluoro-effect).[52] The terminal localised π MO, whose nodal plane is perpendicular to the plane passing through the F atoms, interact effectively with these atoms via the conjugation mechanism. When account is taken of the π−π conjugation, the delocalised b_{3u} and b_{2u} MO with 12 and 12.5 eV binding energies are obtained. Such interpretation of the spectrum agrees with the quantum-chemical calculations (see Basch et al.[52] and the references quoted therein).

The PE spectra of 1,1,4,4-tetrafluoro- and perfluoro-butadienes were used to identify the sequence of the occupied MO in buta-1,3-diene.[53] The sequence $(\ldots 1a_u\pi 7a_g\sigma 1b_g\pi)$, proposed on the basis of the analysis of the spectra, agrees with semiempirical calculations. Non-empirical calculations as well as later calculations by the modified complete neglect of the differential overlap method yields the $7a_g\sigma$ and $1b_g\pi$ order of MO.[54] Analysis of the PE spectra as well as absorption spectra enabled Brundle and Robin[53] to conclude that the carbon skeleton of tetrafluorobutadiene is planar, while perfluorobutadiene is characterised by the rotation of two π-bonds by an angle of 42° about the C−C bond.

Among cyclic compounds with double bonds, we shall mention the fully fluorinated Dewar benzene—hexafluoro[2.2.0]hexa-2,5-diene. In this case, the PE spectra of the fluorinated compound[55,56] were used to demonstrate the absence of interaction between the isolated π-electron systems.

IV. FLUORINE-CONTAINING ALKYNES AND HALOGENO-ALKYNES

The small number of valence electrons in fluorinated acetylenes leads to fairly simple spectra, which have been interpreted reliably by comparison with quantum-chemical calculations.[57–59] It has been

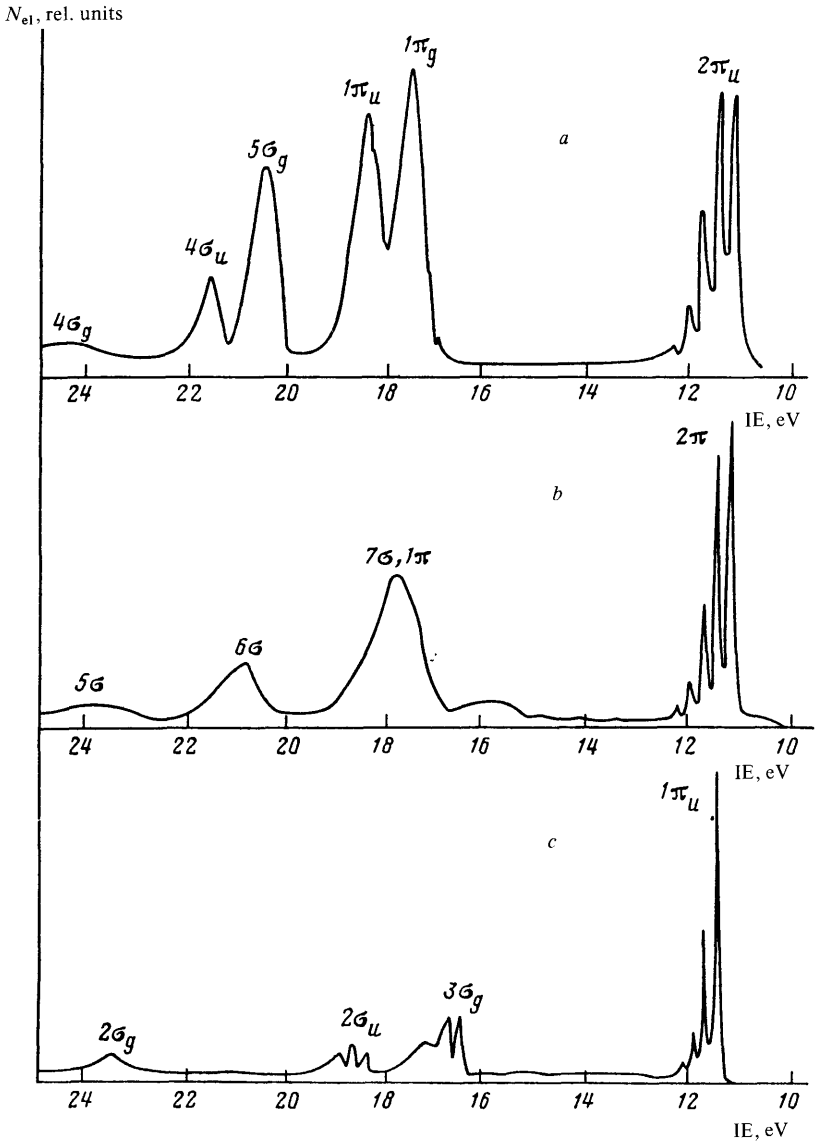


Figure 3. Photoelectron spectra of C_2F_2 (*a*), C_2FH (*b*), and C_2H_2 (*c*).

shown that the HOMO is a C–C bonding MO of the π type with a considerable contribution by the antibonding combination of the $2p\pi$ AO of fluorine (Fig.3). As a result of the cancelling out of the inductive effect and the $n-\pi$ conjugation effect, the first EI of acetylene changes on fluorination by not more than 0.2 eV (the perfluoro-effect). However, approximately the same shift is observed also for the σ(C–H) MO of fluoroacetylene relative to the centre of gravity of two analogous MO of acetylene, which does not agree with a simple treatment of the perfluro-effect. The spectra of other fluorinated alkynes are much more complex and their complete analysis has not been carried out.[9,60–63] In this case, the HOMO are MO of the π type. Fluorination of the methyl groups in propyne and but-2-yne leads to an appreciable (by up to 2.8 eV in perfluorobut-2-yne) increase in the first EI as a result of the inductive influence and negative hyperconjugation.[51]

Similar regularities have been observed also in the spectra of fluorinated dialkynes with conjugated π systems:[9,57,58,60] the fluorination of diacetylene does not change the energy of the HOMO of the π(C≡C) type, but substitution of the hydrogen atoms in the methyl groups of penta-1,3-diyne and hexa-2,4-diyne by fluorine atoms increases appreciably the first EI of their molecules. As an example of the sharp deviation from the usual behaviour of the σ MO on fluorination, we may mention the increase in the EI for the σ(C–C) electron in fluoro- and difluoro-diacetylenes compared with the unsubstituted molecule. This is explained by the interaction of the σ(C–C) MO with the σ(C–H) and σ(C–F) orbitals, the first of which is charactersied by a lower binding energy than the σ(C–C) orbital, while the second is characterised by a higher binding energy.[58]

PES data have been published[61] for the compounds CF_3CCX, where X = Cl, Br, or I. Spin–orbital splitting has been observed in the first bands of bromo- and iodotrifluoropropynes, whose magnitude agrees with the splitting for bromo- and iodoacetylenes[59] and is somewhat smaller than the splitting in the spectra of alkyl halides. This indicates an appreciable $n-\pi$ conjugation in CF_3CCI and CF_3CCBr. Although quantum-chemical calculations have not been made, the HOMO in these two molecules are apparently predominantly np_X AO. For X = Cl, the interaction of the π(C≡C) MO with the p_C AO is weak and the HOMO is in this case an almost pure π(C≡C) MO. The different character of the HOMO for X = Cl and X = Br or I can affect the reactivity of the molecules considered.

V. FLUORINATED AROMATIC COMPOUNDS

Fluorobenzenes have been investigated in greatest detail: the PE spectra have been obtained for different energies of ionising radiation,[9,39,64–66] a thorough analysis of the vibrational structure of the spectra[39] and of the angular distribution of the scattering of photoelectrons removed from different MO [37] has been carried out, and numerous quantum-chemical calculations of the electronic structure have been made.[9,39,54,65,67,68] The PE spectra with excitation by the HeII line have been published[9] for all the fluorobenzenes as well as the results of quantum-chemical calculations taking into account all the valence electrons. In the range of energies less than 25 eV, fluorobenzene has 16 MO according to calculations, but only 11 bands could be resolved in the PE spectra. The situation is still more complex for substituted benzenes with a larger number of fluorine atoms. Despite this, the sequences of the MO quoted[9] are fairly reliable. As an example, we shall quote recommended sequences of MO for fluorobenzene:

$3b_1\pi_{CC}$, $1a_2\pi_{CC}$, $8b_2$, $2b_1\pi_{CC}$, $13a_1$, $7b_2$, $6b_2$, $12a_1$, $5b_2$, $1b_1\pi_F$, $11a_1$, $10a_1$, $4b_2$, $9a_1$, $8a_1$, $3b_2$, $7a_1$, and $6a_1$

and similarly for perfluorobenzene:

$2e_{1g}\pi_{CC}$, $2a_{2u}\pi_{CC}$, $2b_{2u}$, $6e_{2g}$, $1a_{2g}$, $6e_{1u}$, $1b_{2g}\pi_F$, $1e_{2u}\pi_F$, $1e_{1g}\pi_F$, $5e_{2g}$, $1a_{2u}\pi_F$, $5e_{1u}$, $5a_{1g}$, $1b_{2u}$, $4b_{1u}$, $4e_{2g}$, $4e_{1u}$, $4a_{1g}$, $3b_{1u}$, $3e_{2g}$, $3e_{1u}$, and $3a_{1g}$.

In all the fluorobenzenes, the HOMO is the π MO of benzene whose binding energy increases somewhat on fluorination to the maximum value of 9.90 eV in hexafluorobenzene. However, the changes in the first EI on fluorination cannot be accounted for on the basis of the consideration of the conjugation and inductive effects and many-particle calculations are required.[65] Fluoroderivatives of toluene and xylenes have been investigated to a much lesser extent.[65,66,69,70] Detailed analysis of the PE spectra using non-empirical calculations have been carried out and the changes in band intensities in the spectra with excitation by the HeI and HeII lines have been studied only for three $CH_3C_6H_4F$ isomers.[65]

The PE spectra have been obtained and partly identified for a series of fully fluorinated condensed aromatic hydrocarbons[71] as well as 9-fluoroanthracene.[72] For nine substituted anthracenes (apart from fluorine, other halogen atoms as well as CH_3, OCH_3, CHO, etc. were used as substituents), a linear relation has been obtained between the first EI and the Hammett constants.

The comparative analysis of the PE spectra of the *ortho*- and *meta*-substituted benzonorbornadienes carried out by Santiago et al.[73] indicates a different nature of the HOMO in *o*- and *m*-fluorobenzonorbornadienes. The authors attribute the difference between their photochemical activities to this factor.[73]

One of the first studies involving the use of PES to obtain information about the geometrical structure of molecules, is that of Maier and Turner[74] who analysed the spectra of substituted (including seven fluoro-substituted) biphenyls. The difference between the first and fourth EI was used to determine the dihedral angle between the planes of the two benzene groups on the basis of the linear relation $\Delta E = A\cos\theta + B$, where θ is the dihedral angle and A and B are constants. In connection with the hypothesis that the physiological activity of certain biphenyl derivatives (namely chloro-derivatives) is determined by the degree of coplanarity of the molecules, this question has been recently re-examined[75] using new electron diffraction and PES data.

The introduction of chlorine, bromine, and iodine atoms into perfluorobenzene leads to the changes in the PE spectra already examined: the splitting of the first band as a result of the removal of the degeneracy of the HOMO e_{1g} with some decrease (to 0.5 eV for the iodine atom) in the first EI and the appearance of the bands due to the unshared electron pairs of the halogen in the range 11 to 12.5 eV, which is free from bands in the PE spectra of perfluorobenzene.[8,68,76] The sequence of the first five MO in C_6F_5X, namely $a_2\pi$, $b_1\pi$, b_2h_x, $b_1\pi$ (for X = Cl, we have $b_1\pi$, b_2h_{Cl}), π, has been fairly reliably established and confirmed by quantum-chemical calculations.[8,68] The PE spectra of 52 fluorinated compounds containing more than one chlorine or bromine atom, excited by the HeI and HeII lines, as well as the symmetry types of the highest (up to 6) MO, obtained from non-empirical calculations, have been published;[8] they have not so far been analysed. The PE spectra of the *m*-, *p*-, and *o*-isomers of the chloro- and bromo-derivatives of ααα-trifluorotoluene are similar and the first four EI of the different isomers differ by not more than 0.15 eV.[7,66] The first two bands in the spectra correspond to the removal of π electrons and the next two to the removal of the electrons of the unshared pairs of chlorine and bromine.

VI. FLUORINATED ORGANIC COMPOUNDS CONTAINING NITROGEN, OXYGEN, AND SULPHUR HETEROATOMS

Among nitrogen-containing compounds, fluoro-derivatives with the CN group have been investigated in fair detail. The PE spectra of FCN excited by the HeI and HeII lines and the correlation diagram for the first four EI of XCN, where X = I, Br, Cl, or F, have been published.[77] Comparison of the PE spectra of the more complex $CH_2F-C\equiv N$ and $CH_2F-C\equiv CH$ molecules made it possible to assign the bands in the $CH_2F-C\equiv N$ spectrum,[62] although the assignment cannot be regarded as unambiguous because the PE spectrum of $CH_2F-C\equiv N$ is fairly complex owing to the superposition of the bands of the triple bond and the unshared electron pair of the nitrogen atom. For a more accurate interpretation of the spectrum, non-empirical calculations were carried out. The PE spectra, excited by the HeI and HeII lines, of a series of compounds of the type $X-C\equiv C-C\equiv N$, where X = CF_3, F, Cl, Br, or I, have been published.[61] Fig.4 presents the correlation diagram for the EI of cyanoacetylenes on the basis of which the bands in the PE spectra of these substances were assigned. For the bromo-, chloro-, and iodoacetylenes, a strong interaction of the $1\pi_\lambda$ and $2\pi_\lambda$ orbitals is observed. It has been shown that calculations using Green functions predict much better the band sequence and the trend in the variation of EI of cyanoacetylenes than the calculations in terms of the Koopmans approximation.[61]

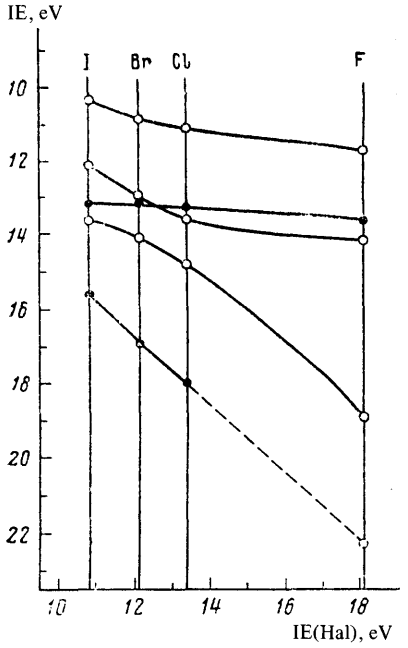


Figure 4. Correlation diagram for the ionisation energies of cyanoacetylenes $X-C\equiv C-C\equiv N$ as a function of the ionisation energy of the halogen atom X = I, Br, Cl, or F.

Comparison of the angular distributions of the photoelectrons, formed on photoionisation of pyridine, pentafluoropyridine, and 2,6-lutidine by the HeI line, made it possible to refine the assignment of the bands in the PE spectrum of pyridine.[78] Thus the first pyridine band was assigned to the a_1n MO, while the fifth band corresponds to the lowest occupied $b_1\pi$ Mo. The asymmetry parameter β of the angular distribution of photoelectrons for pentafluoropyridine hardly changes (in contrast to pyridine and 2,6-lutidine) within the limits of the first band and differs only slightly for different bands: for bands 1–5, β = 0.60, 0.68, 0.65, 0.55, and 0.34 respectively.

The UV absorption spectra and the PE spectra of $(CF_3)_2C=NH$ and other hydrocarbons with the azomethine group have been compared[79] and it has been observed that fluoro-substitution leads to a significant shift, by more than 2 eV, of the n, π, and the first σ ionisation energies for $(CF_3)_2C=NH$ compared with the analogous hydrocarbons. On the other hand, the $\pi^* \leftarrow n$ band shift of the absorption spectra of the corresponding compounds is hardly observed.

Staley et al.[80] used the EI of fluoramines, measured by the PES method, to determine the homolytic dissociation energies of protonated molecules (B), while the difference between the influences of alkyl and fluoroalkyl substitutents on the electronic structure of amines was used to account for the irregularities in the variation of the proton affinities and the values of $D(B^+-H)$ for the test compounds.

The PE spectra of benzonitrile, 1,2- and 1,4-dicyanobenzenes, and their perfluoro-analogues have been studied in detail.[81] The CNDO, INDO, and the linear combination of bond orbital methods were used to assign the bands. It was observed that the difference between the changes in the energies of the σ and π orbitals of benzonitrile on perfluorination is significantly greater than for 1,2- and 1,4-dicyanobenzenes. The fluorescence of perfluorobenzonitrile ions has been observed and investigated;[69] fluorescence has not been observed for benzonitrile itself. The difference is explained by the fact that perfluorination of benzonitrile alters the sequence of the close lying γ^{-1} and π^{-1} ($\tilde{B}$ and $\tilde{C}$) states of the cations.

The study of the influence of the position of fluorine on the PE spectra of fluoroanilines[65] showed that the position of the band corresponding to the removal of an electron from the b_1 MO, in which the contribution by the n_N AO predominates, hardly changes on fluorination in the *ortho*-, *meta*-, and *para*-positions. On the other hand, the HOMO, which is predominantly of the π type, shifts on fluorination towards higher energies, the shift being particularly marked for *meta*-fluoroaniline.

An increase in the number of atoms in a compound usually entails a sharp increase in the complexity of the PE spectrum. However, for molecules with multiple bonds and heteroatoms, the first bands in the PE spectrum are frequently well differentiated. Fig.5 presents the PE spectra of indole and 4,5,6,7-tetrafluoroindole.[82] Fluorination shifts the first four bands by 0.72, 0.60, 0.56, and 0.44 eV respectively and leads to the separation of the fourth band from the remaining group of strongly overlapping bands. The PE spectra of diazanaphthalenes and their fluoro-derivatives have been published.[83] The results of quantum-chemical calculations by the extended Hückel method were used for analysis. Attempts to apply the methods of perturbation theory within the framework of the model involving interactions through the bonds between localised orbitals of the unshared pairs of nitrogen for the description of the splitting of the MO with a considerable contribution by the h_N AO proved unsuccessful for compounds of this class.

Among oxygen- and fluorine-containing hydrocarbons, carbonyl compounds have been studied in greatest detail. The first and second bands in the PE spectra of substituted aldehydes and ketones

usually correspond to the unshared pair of oxygen and the π orbital of the C=O bond. A correlation analysis of the PE spectra of H_2CO, HFCO, and F_2CO has been carried out.[84] The bands in the HFCO spectrum are located in the centre between the corresponding bands of H_2CO and F_2CO. For the carbonyl halides $X_2C=O$, the band of the unshared electron pair of oxygen shifts upwards in the sequence X = H, Br, Cl, F. The first EI of oxalyl halides $(COX)_2$ corresponds to the LEP of the oxygen atom and increases in the sequence X = Br, Cl, F.[85] For $(COBr)_2$ and $(COCl)_2$, groups of four sharp peaks, corresponding to the unshared electron pairs of Br and Cl, are observed at 11.7 and 12.7 eV. A similar sharp structural group is not observed for $(COF)_2$. Comparison of the PES data, the results of the CNDO semiempirical calculation, and the temperature variation of the PE spectra led to the conclusion that these compounds have two isomers. Comparison of the PE spectra of ten chlorofluoroacetones with semiempirical CNDO/2 calculations[86] permitted the assignment of the bands in the PE spectra. The first EI of all the compounds correspond to the removal of one electron of the LEP of oxygen. The second EI for fluoroacetones corresponds to the removal of electrons from the π orbital of the C=O bond, while for chlorofluoroacetones there are several orbitals corresponding to the LEP of chlorine between the above two orbitals.

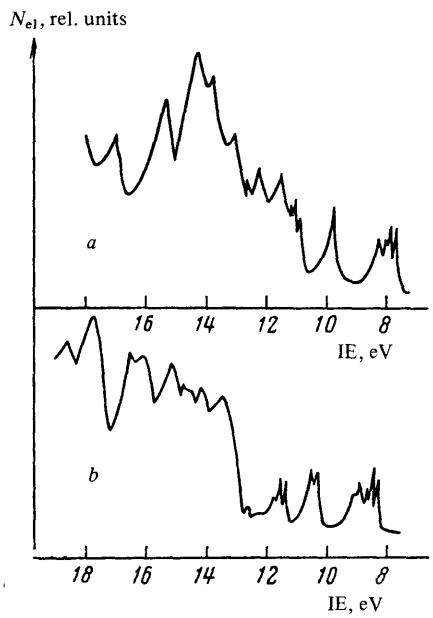


Figure 5. Photoelectron spectra of indole (*a*) and tetrafluoroindole (*b*).

Studies on the PE spectra, excited by the HeI line, of a series of fluoroethers[87] or the type $F[CF(CF_3)CF_2O]_nCHFCF_3$, where $n = -4$ (the E-1, E-2, E-3, and E-4 Freons) showed that they have EI higher by 3.5 eV than the corresponding ordinary ethers. Their vacuum UV absorption spectra begin at energies greater than 10 eV. Both photoelectron and UV spectra are complex, which indicates the existence of several close orbitals of the LEP of oxygen. The EI corresponding to the unshared electron pairs of oxygen and the C–C orbitals must lie close to one another in the region of low EI. The remaining orbitals are difficult to identify from the spectra, since the PE spectra of these compounds are continuous without very distinct bands.

A correlation analysis has been carried out[88,89] and the PES data for *p*-benzophenone and its fluoro-analogues have been compared with the semiempirical calculations by the CNDO/2 and CNDO/S methods. The MO energies have been determined for *p*-benzophenone and have been found to decrease in the sequence $n > n_+ > \pi_+ > \pi_-$, the sequence for *p*-perfluorobenzophenone being $n_+ > n_- > \pi_- > \pi_+$. The perfluoro-effect for these compounds leads to a shift of the *n* orbitals by ~1 eV; the shift of the π orbitals is significantly smaller than that of the *n* orbitals.

The first bands in the PE spectra of fluorine-containing thiocarbonyl compounds correspond, like those for carbonyl compounds, to the LEP of the sulphur atom with a lower EI than for oxygen, while the second band corresponds to the π orbitals of the C=S bond. The bands in the PE spectra of $F_3CS-C(S)-X$, where X = F, Cl, or CF_3, have been assigned on the basis of correlation analysis relative to the PE spectra of halogen-containing carbonyl compounds.[90] Among all the compounds examined, only $F_2C=S$ undergoes $\sigma-\pi$ polarisation. It has been observed that the use of a chlorine atom or the CF_3 group as the substituent results in identical shifts of the PE spectral bands.

The formula relating the first EI of the unshared electron pair of sulphur to the sum of the electronegativities X_α of the substituents has been found from the analysis of the PE spectra of the sulphuranes CF_3SF_3, $(CF_3)_2SF_2$, $(CF_3)_2S$, and others:[91]

$$EI(n_S) = 0.73(\Sigma X_\alpha + 7.10)\ \text{eV}.$$

The outer valence levels in the phenyl and pentafluorophenyl derivatives of bivalent sulphur have been investigated by PES.[92] It has been established earlier for these compounds by X-ray fluorescence spectroscopy that, on passing from phenyl to pentafluorophenyl derivatives of bivalent sulphur, the 3*p* electrons are displaced from conjugation with the aromatic π system, forming a virtually nonbonding level. At first sight, this should promote reactions in which the sulphur atom behaves as a π-electron donor. However, in reality the reactivity of the compounds C_6F_5SX in such reactions is significantly lower than that of their hydrocarbon analogues. The absence of this effect is explained by the increase in EI as a result of the perfluoro-effect.

The influence of the substituents on the EI of the outer occupied molecular orbitals has been investigated for certain groups of compounds containing oxygen and sulphur of the type $X-C_6H_4-Y$, where X is a halogen or another group and Y is a group containing sulphur or oxygen.[93–95] For all the series of compounds, the stabilisation of the HOMO was greatest on substitution of X by fluorine.

With increase in the size of the molecule, the interpretation of the spectrum usually becomes much more complicated owing to the diffuseness of the spectrum and the difficulties in calculations for many-electron systems. However, in many instances the high symmetry of the molecules makes it possible to diminish these difficulties. An example is provided by a comparative study of the PE and vacuum UV absorption spectra of tetrathiofulvalene and related compounds, including tetrakis(trifluoromethyl)tetrathiofulvalene,[96]

where the use of a simple theoretical model and semiempirical calculations made it possible to determine fairly satisfactorily the sequence of orbitals in these compounds.

Ionisation potentials (IP) of fluorine-containing hydrocarbons determined by the EPS method.

Compound	IP, eV	Refs.
C_2F_2	11.18 ± 0.2 a	[58]
"	11.60 v	[9]
C_4F_2	10.05 ± 0.02 a	[58]
"	10.35 v	[9]
CF_4	15.56 ± 0.01 a	[97]
"	16.25 ± 0.04 v	[98]
C_2F_4	10.12 ± 0.01 a	[40]
"	10.56 ± 0.02 v	[36]
$CF_2=C=CF_2$	10.88 a	[5]
"	11.24 v	[50]
$CF_2=C=C=CF_2$	9.30 v	[50]
$CF_3C\equiv CC\equiv CF$	10.58 a	[9]
"	10.85 v	[9, 57]
C_2F_6	14.6 v	[25]
$CF_3CF=CF_2$*	10.60 ± 0.03 a	[40]
"	11.29 v	[43]
Cyclo-C_3F_6*	11.18 ± 0.03 a	[40]
$CF_2=CFCF=CF_2$	9.5 a	[53]
"	10.4 v	[53]
$CF_3C\equiv CCF_3$	12.35 ± 0.01 a	[60]
$CF_3C\equiv C-C\equiv CCF_3$	10.99 ± 0.01 a	[60]
Hexafluorobenzene	9,905 a	[9]
"	10.14 v	[68]
Hexafluorobicyclo[2.2.0]hexa-2,5-diene	10.4 v	[55]
"	10.38 ± 0.01	[56]
C_3F_8	13.38 v	[99]
cis-2-C_4F_8	11.46 v	[42]
trans-2-C_4F_8	11.55 v	[42]
Octafluorotoluene	9.9 ± 0.1 a	[69]
Octafluoronaphthalene	8.85 a	[100]
"	9.05 v	[100]
Octafluoroacenaphthylene	9.1 ± 0.1 v	[71]
Perfluoro-*p*-xylene	9.9 ± 0.1 a	[69]
Decafluoro-1,1-biphenyl	9.40 ± 0.02 a	[74]
"	9.80 v	[74]
Decafluoroanthracene	8.28 ± 0.05 a	[71]
Decafluorophenanthrene	8.75 ± 0.05 a	[71]
"	8.9 v	[71]
Decafluoropyrene	8.36 ± 0.05 a	[71]
$(CF_3)_2C=C(CF_3)_2$	12.61 v	[71]
$CF_2=CF(CF_2)_3CF_3$*	10.48 ± 0.02 a	[101]
$(CF_3)_2C=C=C(CF_3)_2$	12.28 v	[102]
C_2HF	11.26 ± 0.02 a	[58]
"	11.50 v	[9]
CH_3F	12.533 ± 0.006 a	[103]
"	13.038 ± 0.003 v	[103]
C_2H_3F*	10.363 ± 0.015 a	[104]
"	10.56 ± 0.02 v	[36]
C_2H_5F	12.43 v	[105]
$CH_2FC\equiv CH$	10.95 v	[62]
$CH_2=CHCH_2F$	10.11 a	[44]
"	10.38 ± 0.02 v	[45]
$(CH_3)_2CHF$*	11.05 ± 0.02 a	[106]
n-C_3H_7F	11.96 v	[23]
$CF\equiv CC\equiv CH$	10.10 ± 0.02 a	[58]
"	10.25 v	[58]
C_6H_5F*	9.200 ± 0.005 a	[40]
"	9.37 v	[24]
$C_6H_5CH_2F$**	9.12 ± 0.02 a	[107]
"	9.55 v	[108]
o-Fluorotoluene**	8.915 ± 0.01 a	[101, 107]
"	8.93 a	[65]
m-Fluorotoluene**	8.92 ± 0.01 a	[101, 107]
p-Fluorotoluene**	8.78 ± 0.01 a	[101, 107]
"	8.90 a	[65]
2-Fluoroadamantane	9.46 ± 0.05 a	[109]
"	9.85 v	[109]
o-Fluoronorbornadiene	8.66 ± 0.05 v	[73]
m-Fluoronorbornadiene	8.62 ± 0.05 v	[73]
2-Fluoro-1,1-biphenyl	8.20 ± 0.02 a	[74]
4-Fluoro-1,1-biphenyl	8.00 ± 0.02	[74]
11-Fluoro-1,6-methano[10]annulene	8.10 v	[110]
9-Fluoroanthracene	7.46 ± 0.03 v	[72]
2-Fluoroadamantane	9.86 v	[5]
"	9.46 ± 0.05 a	[5, 109]
CH_2F_2	12.72 a	[5, 17]
"	13.29 v	[5]
CD_2F_2	12.79 a	[17]
$CH_2=CF_2$	10.29 ± 0.01 a	[111]
"	10.69 ± 0.02 v	[36]
cis-CHF = CHF	10.23 ± 0.02 a	[37]
"	10.44 ± 0.02 v	[36]
trans-CHF = CHF	10.21 ± 0.02	[37]
"	10.38 ± 0.02 v	[36]
CH_3CHF_2	11.864 ± 0.029 a	[112]
"	12.8 v	[25]

Table (contd.).

Compound	IP, eV	Refs.
$CF_2=C=CH_2$	9.79 ± 0.03 a	[51]
1,2-Difluorobenzene**	9.30 a	[113]
"	9.60 ± 0.03 v	[114]
1,3-Difluorobenzene**	9.35 a	[113]
"	9.60 ± 0.03 v	[114]
1,4-Difluorobenzene**	9.18 a	[113]
"	9.4 v	[9]
$CH_3CF_2CH_3$*	11.42 ± 0.02	[106]
$C_6H_5CHF_2$	9.45 ± 0.02 a	[107]
11,11-Difluoro-1,6-methano[10]annulene	8.19 v	[110]
Difluoromethylenecyclohexane	8.84 a	[115]
2,2'-Difluoro-1,1'-biphenyl	8.35 ± 0.02 a	[74]
"	8.85 v	[5]
3,3'-Difluoro-1,1'-biphenyl	8.35 ± 0.02 a	[74]
"	8.70 v	[5]
4,4'-Difluoro-1,1'-biphenyl	8.00 ± 0.02	[74]
"	8.38 v	[5]
CHF_3*	14.19 ± 0.02 a	[116]
"	14.8 v	[9]
C_2HF_3	10.14 ± 0.02 a	[37]
"	10.54 ± 0.02 v	[36]
CH_3CF_3	13.8 v	[25]
$CF_3C\equiv CH$	11.96 a	[61]
"	12.1 v	[9]
1,2,3-Trifluorobenzene	9.7 v	[9]
1,2,4-Trifluorobenzene**	9.37 ± 0.02 a	[107, 117]
"	9.5 v	[9]
1,3,5-Trifluorobenzene	9.64 a	[37]
"	9.8 v	[9]
Trifluoromethylbenzene***	9.69 ± 0.03 a	[40]
"	9.90 v	[66]
1,3,5-Trifluoro-2,4,6-trimethylbenzene	8.76 ± 0.02 v	[69]
ααα-Trifluoromethylcyclohexane	10.46 ± 0.02	[101]
$CF_2=CHCH=CF_2$	8.98 a	[53]
"	9.38 v	[53]
1,2,3,4-Tetrafluorobenzene	9.56 a	[64]
"	9.78 v	[37]
1,2,3,5-Tetrafluorobenzene	9.56 a	[64]
"	9.6 v	[9]
p-Fluoro-ααα-trifluorotoluene	9.69 ± 0.02 a	[107]
1,2,4,5-Tetrafluorobenzene	9.36 a	[64]
"	9.5 v	[9]
1,2,4,5-Tetrafluoro-2-methylbenzene	9.16 ± 0.02 a	[69]
Pentafluorobenzene**	9.82 a	[118]
"	9.64 a	[64]
"	9.90 v	[68]
Pentafluoromethylbenzene	9.4 ± 0.1 a	[69]
"	9.81 v	[68]
$C_6F_5CH=CH_2$	9.18 ± 0.02	[119]
2,2,3,3,8,8,9,9-Octafluorotricyclo[8.2.2.2]-hexadeca-4,6,10,12,13,15-hexaene	8.90	[120]
CF_3Cl*	12.39 a	[121]
"	12.60 ± 0.02 a	[116]
CF_3Cl*	13.08 ± 0.01 v	[27]
C_2F_3Cl**	9.76 a	[47]
"	9.82 a	[63]
"	10.24 ± 0.01 v	[49]
$CF_3C\equiv CCl$	11.14 ± 0.02 a	[61]
"	11.29 v	[61]
CF_3CF_2Cl	12.96 v	[26]
C_6F_5Cl	9.72 ± 0.02 a	[8]
"	9.94	[68]
CF_2Cl_2*	11.75 a	[122]
"	11.87 ± 0.02 a	[116]
"	12.24 v	[27]
$CF_2=CCl_2$	9.62 a	[63]
"**	9.69 ± 0.01 a	[123]
"	9.84 v	[137]
CF_2Cl-CF_2Cl	12.47 v	[32]
"	12.85 v	[26]
$CF_3CCl=CClCF_3$*	10.36 ± 0.01 a	[101]
"	10.55 ± 0.03 v	[43]
$CFCl_3$	11.46 ± 0.02 a	[116]
"	11.76 ± 0.01 v	[27]
CF_3CCl_3*	11.78 ± 0.03 a	[101]
$CFCl_2CF_2Cl$	12.05 v	[26]
1,3,5-Trichloro-2,4,6-trifluorobenzene	9.48 ± 0.02 a	[8]
"	9.68 ± 0.02 v	[8]
CH_2FCl	11.74	[28]
"	11.9 v	[5]
$CH_2=CFCl$**	9.97 a	[47]
1-Chloro-2-fluorobenzene	9.18 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
1-Chloro-3-fluorobenzene	9.22 ± 0.02 a	[8]
"	9.40 ± 0.02 v	[8]
1-Chloro-4-fluorobenzene	9.24 ± 0.02 v	[8]
"	9.08 ± 0.02 a	[8]
CHF_2Cl*	12.28 ± 0.02 a	[116]
"	12.56 ± 0.05 v	[12]
trans-CHF = CFCl	9.83 ± 0.02 a	[48]
cis-CHF = CFCl	9.86 ± 0.02 a	[48]
$CF_2=CHCl$**	9.76 a	[47]
"	9.84 a	[49]
"	10.04 ± 0.01 v	[49]
$CH_2=CFCl$	9.97	[47]
cis-CHCl = CHF	9.87 ± 0.01	[48, 101]
trans-CHCl = CHF	9.87 ± 0.07	[48, 101]
CH_3CF_2Cl	11.93 ± 0.01 a	[101]
"	12.50 v	[26]

Table (contd.).

Compound	IP, eV	Refs.
1-Chloro-2,4-difluorobenzene	9.17 ± 0.02 a	[8]
"	9.35 ± 0.05 v	[8]
1-Chloro-3,5-difluorobenzene	9.40 ± 0.02 a	[8]
"	9.66 ± 0.02 v	[8]
1-Chloro-2,6-difluorobenzene	9.37 ± 0.02 a	[8]
"	9.53 ± 0.02 v	[8]
1-Chloro-2,5-difluorobenzene	9.19 ± 0.02 a	[8]
"	9.40 ± 0.05 v	[8]
1-Chloro-3,4-difluorobenzene	9.24 ± 0.02 a	[8]
"	9.40 ± 0.05 v	[8]
1-Chloro-2,3,4-trifluorobenzene	9.42 ± 0.02 a	[8]
"	9.59 ± 0.02 v	[8]
1-Chloro-2,4,5-trifluorobenzene	9.27 ± 0.02 a	[8]
"	9.40 ± 0.05 a	[8]
1-Chloro-2,3,6-trifluorobenzene	9.39 ± 0.02 a	[8]
"	9.60 ± 0.02 v	[8]
1-Chloro-2-trifluoromethylbenzene	9.47 a	[7]
1-Chloro-3-trifluoromethylbenzene	9.50 a	[7]
1-Chloro-4-trifluoromethylbenzene	9.56 a	[7]
"	9.80 v	[66]
1-Chloro-2,3,5,6-tetrafluorobenzene	9.58 ± 0.02	[8]
"	10.05 ± 0.05 v	[8]
$CF_3CF_2CF_2CH_2Cl$	10.84 ± 0.02 a	[101]
$CHFCl_2$*	11.75 ± 0.02 a	[116]
"	11.92 ± 0.05 v	[12]
1,2-Dichloro-3-fluorobenzene	9.29 ± 0.02 v	[8]
1,2-Dichloro-4-fluorobenzene	9.16 ± 0.02 a	[8]
"	9.31 ± 0.02 v	[8]
1,3-Dichloro-2-fluorobenzene	9.32 ± 0.02 a	[8]
"	9.32 ± 0.02 v	[8]
1,5-Dichloro-2-fluorobenzene	9.39 ± 0.02 v	[8]
1,4-Dichloro-3-fluorobenzene	9.09 ± 0.02 a	[8]
"	9.28 ± 0.02 v	[8]
2,4-Dichloro-1-fluorobenzene	9.12 ± 0.02 a	[8]
"	9.31 ± 0.02 v	[8]
1,2-Dichloro-3,4-difluorobenzene	9.33 ± 0.02 a	[8]
"	9.50 ± 0.02 v	[8]
1,3-Dichloro-2,4-difluorobenzene	9.27 ± 0.02 a	[8]
"	9.50 ± 0.05 v	[8]
1,3-Dichloro-2,5-difluorobenzene	9.32 ± 0.02 a	[8]
"	9.55 ± 0.05 v	[8]
1,4-Dichloro-2,5-difluorobenzene	9.17 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
2,3-Dichloro-1,4-difluorobenzene	9.32 ± 0.02 a	[8]
"	9.50 ± 0.02 v	[8]
$CF_2ClCHFCl$	12.00 v	[26]
2,4-Dichloro-1,3,5-trifluorobenzene	9.37 ± 0.02 a	[8]
"	9.57 ± 0.02 v	[8]
1,2,3-Trichloro-6-fluorobenzene	9.20 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
1,2,5-Trichloro-4-fluorobenzene	9.16 ± 0.02 a	[8]
"	9.31 ± 0.02 v	[8]
1,3,5-Trichloro-2-fluorobenzene	9.23 ± 0.02 a	[8]
"	9.50 ± 0.02 v	[8]
2,3,5-Trichloro-1-fluorobenzene	9.24 ± 0.02 a	[8]
"	9.40 ± 0.02 v	[8]
1,2,3,4-Tetrachloro-6-fluorobenzene	9.20 ± 0.02 a	[8]
"	9.34 ± 0.02 v	[8]
2,3,5,6-Tetrachloro-1-fluorobenzene	9.19 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
"	9.34 ± 0.02 v	[8]
CF_3Br*	11.76 ± 0.02 a	[116]
"	12.12 ± 0.02 v	[29]
C_2F_3Br	9.67	[63]
"	10.11 ± 0.03 v	[43]
$CF_3C \equiv CBr$	10.81 ± 0.02 a	[61]
C_6F_5Br	9.67 ± 0.02 a	[8]
"	9.8 v	[76]
CF_2Br_2*	10.98 ± 0.02 a	[116]
"	11.17 ± 0.05	[13]
CF_2BrCF_2Br	11.44 ± 0.01 v	[32]
1,2-Dibromo-3,4,5,6-tetrafluorobenzene	9.50 ± 0.02 v	[8]
1,3-Dibromo-2,4,5,6-tetrafluorobenzene	9.45 ± 0.02 v	[8]
1,4-Dibromo-2,3,5,6-tetrafluorobenzene	9.42 ± 0.02 v	[8]
$CFBr_3$	10.67 ± 0.01 a	[101]
"	10.70 ± 0.05	[13]
1,3,5-Tribromo-2,4,6-trifluorobenzene	9.33 ± 0.02 a	[8]
cis-CHF = CHBr	9.75 v	[43]
CH_2FCH_2Br (*gauche*)	10.57 v	[33]
CH_2FCH_2Br (*trans*)	10.77 v	[33]
$CH_2FCH_2CH_2Br$	10.38 v	[33]
CH_3CHFCH_2Br (*gauche*)	10.44 v	[33]
CH_3CHFCH_2Br (*trans*)	10.61 v	[33]
$CH_3CH_2CHFCH_2Br$ (*gauche*)	10.32 v	[33]
$CH_3CH_2CHFCH_2Br$ (*trans*)	10.49 v	[33]
$(CH_3)_2CFCH_2Br$ (*gauche*)	10.28 v	[33]
$(CH_3)_2CFCH_2Br$ (*trans*)	10.42 v	[33]
$CH_3CHFCHBrCH_3$ (*erythro, gauche*)	10.19 v	[33]
$CH_3CHFCHBrCH_3$ (*trans*)	10.34 v	[33]
$CH_3CHFCHBrCH_3$ (*threo, gauche*)	10.21 v	[33]
$CH_3CHFCHBrCH_3$ (*trans*)	10.37 v	[33]
1-Bromo-2-fluoro-*cis*-cyclopentene	10.10 ± 0.02	[124]
1-Bromo-2-fluoro-*trans*-cyclopentene	10.25 ± 0.02	[124]
1-Bromo-2-fluorobenzene	9.11 ± 0.02 a	[8]
"	9.14 v	[7]
1-Bromo-2-fluorobenzene	9.11 ± 0.02 a	[8]
"	9.25 v	[7]
1-Bromo-4-fluorobenzene	9.02 ± 0.02 a	[8]
cis-1-Bromo-2-fluorocyclohexane	10.04 ± 0.02 v	[124]

Table (contd.).

Compound	IP, eV	Refs.
trans-1-Bromo-2-fluorocyclohexane	10.18 ± 0.02 v	[124]
"	10.05 v	[33]
4-Bromo-4′-fluoro-1,1′-biphenyl	8.10 ± 0.02 a	[74]
"	8.40 v	[5]
1-Bromo-2,4-difluorobenzene	9.16 ± 0.02 a	[8]
1-Bromo-2,5-difluorobenzene	9.18 ± 0.02 a	[8]
"	9.38 ± 0.02 v	[8]
1-Bromo-3,4-difluorobenzene	9.19 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
1-Bromo-2,4,5-trifluorobenzene	9.25 ± 0.02 a	[8]
"	9.42 ± 0.02 v	[8]
1-Bromo-2,4,6-trifluorobenzene	9.34 ± 0.02 v	[8]
1-Bromo-2-trifluoromethylbenzene	9.38 a	[7]
1-Bromo-3-trifluoromethylbenzene	9.36 a	[7]
1-Bromo-4-trifluoromethylbenzene	9.48 a	[7]
"	9.55 v	[66]
1-Bromo-2,3,4,6-tetrafluorobenzene	9.50 ± 0.02 a	[8]
"	9.67 ± 0.02 v	[8]
1-Bromo-2,3,4,5-tetrafluorobenzene	9.46 ± 0.02 a	[8]
"	9.55 ± 0.02 v	[8]
1-Bromo-2,3,5,6-tetrafluorobenzene	9.45 ± 0.02 v	[8]
"	9.85 ± 0.05 v	[8]
2,4-Dibromo-1-fluorobenzene	9.05 ± 0.02 a	[8]
"	9.18 ± 0.02 v	[8]
CF_2BrCH_2Br	10.83 ± 0.01 a	[101]
"	10.86 ± 0.01 v	[32]
$CHFBrCH_2Br$	10.75 ± 0.02 a	[101]
1,2-Dibromo-4,5-difluorobenzene	9.13 ± 0.02 a	[8]
"	9.28 ± 0.02 v	[8]
1,4-Dibromo-2,5-difluorobenzene	9.09 ± 0.02 v	[8]
CF_2BrCl*	11.21 ± 0.02 a	[116]
"	11.51 ± 0.05 v	[13]
CF_3I	10.32 ± 0.03 a	[125]
"*	10.38 ± 0.02 a	[116]
"	10.45 ± 0.05 v	[15]
$CF_3C \equiv CI$	10.17 ± 0.02 a	[61]
C_2F_5I	10.65 v	[34]
C_6F_5I	9.54 v	[68]
"	9.84 v	[34]
CF_2ICF_2I (*trans*)	10.11 ± 0.01 v	[32]
CF_3CF_2I (*gauche*)	10.21 ± 0.01 v	[32]
CF_3CH_2I**	9.998 a	[126]
"	9.99 v	[34]
$CF_3(CF_2)_2CH_2I$	9.96 ± 0.02 a	[101]
FCN	13.34 ± 0.02 a	[77]
"	13.65 v	[77]
CF_3CN	13.86 a	[127]
"	14.3 v	[127]
$CF \equiv CCN$	11.51 ± 0.02 a	[15]
3,3-Difluorodiazirine	11.2 ± 0.05	[100]
$CF_3C \equiv CCN$	12.00 ± 0.002 a	[15]
2,4,6-Trifluoro-1,3,5-triazine	11.5 a	[100]
"	12.3 v	[127]
Tetrafluoropyrazine	10.37 v	[128]
Tetrafluoropyridazine	11.15 v	[128]
Tetrafluoropyrimidine	10.82 v	[128]
1,2-Dicyano-3,4,5,6-tetrafluorobenzene	10.60 v	[81]
1,4-Dicyano-2,3,5,6-tetrafluorobenzene	10.65 v	[81]
Pentafluoropyridine	10.08 a	[127]
"	10.3 v	[127]
Pentafluorobenzonitrile	10.1 a	[69]
"	10.45 v	[81]
cis-$CF_3N = NCF_3$	10.5 a	[38]
trans-1,2-Bis(trifluoromethyl)fumaronitrile	11.85 ± 0.05 v	[129]
Hexafluorocinnoline	9.66 v	[130]
2,3,4,5,6,7-Hexafluoro-1,8-naphthyridine	10.01 v	[83]
1,3,4,5,6,8-Hexafluoro-2,7-naphthyridine	9.50 v	[83]
Hexafluorophthalazine	9.90 v	[130]
Hexafluoroquinazoline	9.43 v	[130]
Hexafluoroquinoxaline	9.65 v	[130]
Heptafluoroisoquinoline	9.29 v	[131]
Heptafluoroquinoline	9.51 v	[131]
$(C_2F_5)_3N$*	11.7 a	[56]
CH_2F-CN	12.67 v	[62]
2-Fluoroaniline*	7.95 ± 0.02 a	[107]
"	8.18 v	[132]
3-Fluoroaniline*	7.90 ± 0.02 a	[107]
"	8.32 v	[132]
4-Fluoroaniline*	7.82 ± 0.02 a	[107]
"	8.18 v	[132]
2-Fluorobenzonitrile	9.78 v	[133]
3-Fluorobenzonitrile	9.79 v	[133]
4-Fluorobenzonitrile	9.74 v	[133]
2-Fluoropyrimidine	10.5 a	[128]
4-Fluoroquinazoline	9.22 v	[83]
2-Fluoroquinazoline	9.15 v	[83]
2,3-Difluoropyrazine	10.35 v	[128]
2,6-Difluoropyrazine	10.30 v	[128]
3,6-Difluoropyridazine	10.17 v	[128]
2,4-Difluoropyrimidine	10.65 v	[128]
4,6-Difluoropyrimidine	10.95 v	[128]
2,7-Difluoropyrimidine-1,8-naphthyridine	9.26 v	[83]
2,4-Difluoroquinazoline	9.30 v	[83]
2,3-Difluoroquinoxaline	9.30 v	[130]
2,6-Difluorophenyliminoimidazoline	8.12 v	[134]
4-(Trifluoromethyl)pyridine	10.1 v	[135]
2,4,6-Trifluoropyrimidine	10.93 v	[128]
4,5,6,7-Tetrafluoro-1*H*-indole	8.30 ± 0.015 v	[82]
1,3,6,8-Tetrafluoro-2,7-naphthyridine	9.55 v	[83]

Table (contd.).

Compound	IP, eV	Refs.
5,6,7,8-Tetrafluoroquinoxaline	9.50 v	[130]
2,3,4,5,6-Pentafluoroaniline	8.40 ± 0.02 a	[136]
2-(Pentafluorophenylimino)imidazoline	8.60 v	[134]
$(CF_3)_2C=NH$	11.8 v	[79]
$(CH_3)_2NC(CF_3)=C(CF_3)H$	8.22 a	[63]
$C_6H_5N(CF_3)_2$	10.0 ± 0.03 a	[66]
F_2CO	13.04 a	[137]
"	13.6 v	[138]
$(COF)_2$	12.20 a	[85]
"	12.58 v	[139]
CF_3OF	12.20 a	[5]
"	13.64 v	[5]
2,3,5,6-Tetrafluorocyclohexa-2,5-diene-1,4-dione	10.96 ± 0.05 v	[88]
$(CF_3)_2CO$	11.44 a	[38]
"	12.09 ± 0.02 v	[86]
$(CF_3)_2CCO$	10.67 a	[102]
Tetrafluoro-*p*-benzoquinone	10.7 a	[127]
Difluoromaleic anhydride	11.45 a	[127]
"	11.7 v	[127]
HFCO	12.37 ± 0.02	[84]
"	12.55 v	[5]
CH_3CFO	11.51 ± 0.02 a	[105]
CH_3COCH_2F	10.20 ± 0.02 v	[86]
Fluoromethyloxiran	10.78 v	[140]
$CH_2FCH_2OCH_3$	10.18 v	[105]
2-Fluorophenol	8.66 ± 0.01 a	[101]
"	8.95 v	[141]
"	8.97 ± 0.02 v	[142]
3-Fluorophenol	8.99 v	[141]
"	9.05 ± 0.02	[142]
4-Fluorophenol	8.77 v	[141]
"	8.79 ± 0.02 v	[142]
p-$CH_2FC_6H_4COOCH_3$*	9.09 a	[143]
C_6H_5COF*	9.78 a	[144]
cis-*m*-Fluoroanisole***	8.4134 a	[145]
trans-*m*-Fluoroanisole***	8.4673 a	[145]
2,4-Difluorophenol	8.98 ± 0.02 v	[142]
2,5-Difluorophenol	9.10 ± 0.02 v	[142]
3,5-Difluorophenol	9.04 ± 0.02 v	[142]
CF_3CH_2OH	11.74 v	[5]
CH_3COCF_3	10.67 ± 0.01 a	[146]
"	11.00 ± 0.02 v	[86]
2,3,4-Trifluorophenol	9.19 ± 0.02 v	[142]
2,4,5-Trifluorophenol	9.10 ± 0.02 v	[142]
CF_3COOH	11.46 a	[147]
"	12.00 ± 0.03 v	[148]
"	12.06 v	[149]
CF_3COOCH_3	11.31 a	[147]
"	11.6 v	[147]
$HCOOCH_2CF_3$	11.31 a	[147]
$C_2H_5OCOCF_3$*	11.07 ± 0.03 a	[150]
$CF_3COOC_2H_5$	11.6 v	[147]
$CH_3COOCH_2CF_3$	10.84 a	[147]
$CF_3COCH_2COCH_3$	9.72 a	[5]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
$(CH_3)_3CCOCH_2COCF_3$	9.87 ± 0.07 v	[151]
iso-C_3H_7COOH-CF_3COOH	10.7 v	[5]
p-$CF_3C_6H_4COOCH_3$*	9.55 a	[143]
m-$CF_3C_6H_4COOCH_3$*	9.60 a	[143]
p-$CF_3COC_6H_4COOCH_3$*	9.64 a	[143]
m-$CF_3CH_2C_6H_4COOCH_3$	9.26 a	[143]
$(CHF_2)_2CO$	11.33 ± 0.02 v	[36]
2,3,5,6-Tetrafluorophenol	9.40 ± 0.02 v	[142]
$C_2F_5CH_2OH$	11.67 v	[5]
C_6F_5OH	9.20 ± 0.02 a	[152]
"	9.37 ± 0.02 a	[102]
$C_6F_5OCH_3$	9.10 ± 0.02 a	[152]
$CF_3CH(OH)CF_3$	12.23 v	[153]
Hexafluorocyclobutanone	11.2 a	[154]
$CF_3CF_2CF_2OCHFCF_3$	12.6 a	[87]
p-$C_2F_5C_6H_4COOCH_3$*	9.66 a	[143]
m-$C_2F_5C_6H_4COOCH_3$*	9.67 a	[143]
$(C_2H_5O)_2C=C=C(CF_3)_2$	8.93 a	[102]
CF_3COOCH_3	11.31 a	[147]
"	11.6 v	[147]
$HCOOCH_2CF_3$	11.31 a	[147]
$C_2H_5OCOCF_3$*	11.07 ± 0.03 a	[150]
$CF_3COOC_2H_5$	11.6 v	[147]
$CH_3COOCH_2CF_3$	10.84 a	[147]
$CF_3COCH_2COCH_3$	9.72 a	[6]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
$(CH_3)_3COOCH_2COCF_3$	9.87 ± 0.07 v	[151]
iso-C_3H_7COO-CF_3COOH	10.7 v	[5]
p-$CF_3C_6H_4COOCH_3$*	9.55 a	[143]
m-$CF_3C_6H_4COOCH_3$*	9.60 a	[143]
p-$CF_3COC_6H_4COOCH_3$*	9.64 a	[143]
m-$CF_3CH_2C_6H_4COOCH_3$	9.26 a	[143]
$(CHF_2)_2CO$	11.33 ± 0.02 v	[86]
2,3,5,6-Tetrafluorophenol	9.40 ± 0.02 v	[142]
$C_2F_5CH_2OH$	11.67 v	[5]
C_6F_5OH	9.20 ± 0.02 a	[152]
"	9.37 ± 0.02 a	[102]

Table (contd.).

Compound	IP, eV	Refs.
$C_6F_5OCH_3$	9.10 ± 0.02 a	[152]
$CF_3CH(OH)CF_3$	12.23 v	[153]
Hexfluorocyclobutanone	11.2 a	[154]
$CF_3CF_2CF_2OCHFCF_3$	12.6 a	[87]
p-$C_2F_5C_6H_4COOCH_3$*	9.66 a	[143]
m-$C_2F_5C_6H_4COOCH_3$*	9.67 a	[143]
$(C_2H_5)_2C=C=C(CF_3)_2$*	8.93 a	[102]
p-$CF_3CF_2CF_2C_6H_4COOCH_3$*	9.59 a	[143]
m-$CF_3CF_2CF_2C_6H_4COOCH_3$*	9.63 a	[143]
p-$(CF_3)_2CFC_6H_4COOCH_3$*	9.60 a	[143]
$CF_2H(CF_2)_3CH_2OC(O)CH_3$*	10.61 ± 0.03 a	[150]
p-$(CF_3)_3CC_6H_4COOCH_3$*	9.54 a	[143]
m-$(CF_3)_3CC_6H_4COOCH_3$*	9.51 a	[143]
p-$(CF_3)_3CCH_2C_6H_4COOCH_3$*	9.20 a	[143]
m-$(CF_3)_3CCH_2C_6H_4COOCH_3$*	9.20 a	[143]
$F[CF(CF_3)CF_2O]_2CHFCF_3$	12.78 v	[87]
$F[CF(CF_3)CF_2O]_3CHFCF_3$	12.96 v	[87]
$F[CF(CF_3)CF_2O]_4CHFCF_3$	13.47 v	[87]
$CClF_2COCF_3$	11.71 ± 0.02 v	[86]
$(CF_2Cl)_2CO$	10.71 v	[146]
$CCl_2FCOCClF_2$	11.21 v	[86]
CF_3COCCl_3	10.80 ± 0.01 a	[146]
"	11.24 v	[86]
$CClF_2COCHF_2$	11.33 ± 0.02 v	[86]
$CH_2BrCOCF_3$	10.92 ± 0.02 v	[86]
CF_3NO	10.4 ± 0.01 a	[155]
"	11.6 ± 0.05 v	[156]
$(CF_3)_2NO$	10.7 ± 0.1 v	[157]
trans-C_4F_9NO	8.55 ± 0.01 a	[155]
4-Fluorobenzamide	9.50 v	[158]
o-Fluoronitrobenzene	9.86 v	[159]
m-Fluoronitrobenzene	9.88 a	[159]
"	10.08 v	[159]
p-Fluoronitrobenzene	9.90 a	[159]
"	10.06 v	[159]
7-Fluoro-3,10-dimethylbenzopteridine-2,4-(3*H*, 10*H*)-dione	8.51 v	[160]
CF_3CONH_2	10.8 a	[127]
"	11.3 v	[127]
4-(Trifluoromethyl)pyridine 1-oxide	8.90 v	[135]
2,2,2-Trifluoro-*N*-phenylacetamide	8.93 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2-methylphenyl)acetamide	8.84 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(3-methylphenyl)acetamide	8.73 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(4-methylphenyl)acetamide	8.61 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,3-dimethylphenyl)acetamide	8.62 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(3,4-dimethylphenyl)acetamide	8.51 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,4-dimethylphenyl)acetamide	8.56 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(3,5-dimethylphenyl)acetamide	8.59 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,5-dimethylphenyl)acetamide	8.70 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,6-dimethylphenyl)acetamide	8.99 ± 0.05 v	[161]
5-Trifluoromethyluracil	10.07 v	[162]
$F_2C=S$	10.45 ± 0.01	[163]
"	10.64 v	[164]
CF_3SF_3	12.4 v	[91]
CF_3SCF_3	11.35 v	[91]
$(CF_3)_2C=C=S$	9.96 a	[102]
$(CF_3)_2SF_2$	12.1 v	[91]
$(C_6F_5)_2S$	9.34 v	[92]
$CF_3SC(F)=S$	10.12 v	[90]
$F_3SCF_2SF_3$	12.1 v	[91]
$(CF_3)_2S_3$	10.16 v	[5]
$(CF_3S)_2C=S$	9.25 v	[90]
$(CF_3)_2S_4$	9.75 v	[5]
$C_6S_4(CF_3)_4$	7.95 v	[165]
Tetrakis(trifluoromethyl)tetrathiofulvalene	7.95 a	[96]
C_6F_5SH	9.50 v	[92]
$CH_2=SF_4$	10.65 v	[166]
$C_6F_5SCH_3$	9.16 v	[92]
5-*p*-Fluorophenyl-1,2-dithiole-3-thione	8.14 v	[167]
FClCS	10.20 v	[164]
C_6F_5SCl	9.73 v	[92]
$S=C(Cl)SCF_3$	9.57 v	[165]
$(CH_3)SO_2(F)$	12.53 v	[168]
"	12.61 v	[169]
$FC_6H_4CH=CHSO_2CH_3$	9.05	[169]
11,11-Difluoro-1,6-methano[10]annulene-2-sulphonyl chloride	8.90 v	[110]
10-[3(4-Methyl-1-piperazinyl)propyl]-2-(trifluoromethyl)-10*H*-phenylthiazine	7.31 ± 0.08 v	

Notation. Ionisation potentials: a = adiabatic, v = vertical.

*Photoionisation mass spectrometry.

**Spectroscopic ionisation method.

***Multiphoton ionisation.

The first adiabatic and vertical ionisation energies of all the fluorine-compounds in the classes dealt with in the review which have been investigated up to 1985 are presented in the Table. As a rule, one most reliable value of the ionisation energy is included for each

molecule. The error in the ionisation energy is quoted only when it is given in the original communication. In the remaining cases, it can be estimated as 0.1 eV for values quoted with a single figure after the decimal point and 0.05 eV for those quoted with two figures after the decimal point. The compounds are listed in the Table in order of increasing numbers of the S, O, N, I, Br, Cl, F, H and C atoms (starting with their absence).

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Thus chlorination of organic compounds increases the ionisation energies of almost all the orbitals. This effect is particularly large for perfluorohydrocarbons and can be used for the specific synthesis of compounds with high ionisation potentials.

The observed regularities in the variation of the ionisation energies of the compounds on replacement of all the hydrogen atoms by fluorine (the perfluoro-effect) provide an effective method for the recognition of the character of the MO in certain classes of compounds, despite its limited applicability. Thus the replacement of hydrogen by fluorine in a planar molecule has a much greater stabilising effect on σ MO than on π MO. This effect is most pronounced for non-aromatic hydrocarbons whose fluorination shifts the π MO by 0–0.5 eV and the σ MO by 2–3 eV. For aromatic compounds, the shift of the π orbitals can be somewhat greater. Analysis of a large number of PE spectra demonstrated that detailed analysis of the electronic mechanism which leads ultimately to the perfluoro-effect is fairly complex. This is because, when hydrogen is replaced by fluorine, two competing influences are observed: the greater electronegativity of the fluorine atoms, leading mainly to the polarisation of the σ-skeleton of the molecule, and the repulsive interaction of the unshared electron pairs of fluorine with the π-system to which they are linked. In studying the influence of the perfluoro-effect, it is essential to take into account the molecular symmetry.

The PE spectra of organofluorine compounds differ greatly from the spectra of other halogen-substituted compounds. This is associated with the following properties of the fluorine atom, which distinguish it among the halogens. Firstly, the C–F bonds are appreciably shorter than the C–X bonds, where X = Cl, Br, or I. If the sum of the covalent atomic radii is used to estimate the length of these bonds, then 1.4, 1.7, 1.9, and 2.1 Å are obtained for F, Cl, Br, and I respectively. Secondly, the 2*p* AO of fluorine is smaller (less diffuse) than the AO of the valence *p* electrons of the remaining halogens. Such properties lead to an effective interaction of the AO of fluorine with the MO of the C–C and C–X bonds which have the correct symmetry and hence to an appreciable delocalisation of the unshared electron pairs of fluorine. Therefore the PE spectra of organofluorine compounds do not contain the narrow bands characteristic of the unshared electron pairs of the other halogens. In many instances, there is probably no point at all in considering the unshared electron pairs of fluorine. The differentiation of the corresponding bands in the PE spectrum is a very complex task, especially if account is taken also of the small spin–orbital splitting of these bands. For the other halogens, the spin–orbital splitting is manifested reliably in the spectra and is a satisfactory diagnostic feature for the identification of the bands corresponding to the removal of the electrons of the unshared pairs.

Yet another important difference between the PE spectra of organofluorine compounds and those of other organic substances is the lower frequencies of the corresponding vibrations of the ions when hydrogen atoms are replaced by fluorine. Thus the energies of the vibrational quanta for the stretching vibrations of the C–H and C–F bonds are approximately 3000 and 1300 cm^{-1} respectively. Such a marked change in frequency can alter significantly the shape of the individual bands in the PE spectra, especially when the vibrational structure is resolved.

In comparing the ionisation energies obtained from the PE spectra with theoretical calculations, preference should be given to many-body calculations of ionisation energies. Semiempirical calculations can in certain cases yield appreciably different arrangement of orbitals, especially for different isomers.

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Oxidative Substitution of Halogen Atoms in Organic Halogeno-derivatives—a New Type of Nucleophilic Substitution Reactions at a Saturated Carbon Atom

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The review surveys and gives a systematic account of data on the oxidative substitution of halogen atoms in organic halogeno-derivatives. The stereochemistry of the reactions as well as numerous rearrangements occurring on oxidative substitution are considered. The influence of the substituted halogen (Cl, Br, or I), the substituents at the reaction centre, and the oxidant on the character of the products and the reaction mechanism is demonstrated.
The bibliography includes 97 references.

CONTENTS

I. Introduction 760
II. Reactions of alkyl iodides and bromides with Cl_2, Br_2, and ICl 760
III. Reactions of alkyl halides with nitric acid and other inorganic oxidants 761
IV. Reactions of alkyl iodides with organic peroxy-acids 763
V. Interaction of alkyl halides with hypohalite derivatives of strong acids 766
VI. Interaction of alkyl halides with halogen fluorides 768
VII. The mechanism of the oxidative substitution 771

I. INTRODUCTION

During the last decade, numerous reactions of alkyl halides with oxidising agents under mild conditions, leading to the exchange of a halogen for another nucleophilic residue and to the oxidation of the halogen eliminated to the molecular form Hal_2 or heteroatomic molecules containing the oxidised halogen, have attracted the attention of investigators:

$$RI + HNO_3 \rightarrow RONO_2 + I_2 , \quad (1)$$

$$RBr + HNO_3 \xrightarrow{HF} RF + Br_2 , \quad (2)$$

$$RI + ArCO_3H \xrightarrow{H_2O} ROH + I_2 + I_2O_5 , \quad (3)$$

$$RCl + ClOSO_2F \rightarrow ROSO_2F + Cl_2 , \quad (4)$$

$$RBr + ClF \rightarrow RF + BrCl . \quad (5)$$

Sverlakov and co-workers, who discovered such reactions in a study of the nitrolysis of halogenoalkanes with nitric acid [Eqns.(1) and (2)], who proposed an apt name, from our point of view, for reactions of this type—oxidative substitution.

Interest in these reactions has been aroused for several reasons. Thus it has been suggested that reactions of an analogous type occur in the metabolism of alkyl halides in the living organism [Eqn.3], which is the reason for the carcinogenic properties of certain halogenoalkanes. On the other hand, the introduction by this procedure into highly halogenated substrates of an oxygen-containing functional group [Eqn.(4)] or the fluorine atom [Eqn.(5)] by treatment with powerful oxidants such as chlorine fluorosulphonate, chlorine monofluoride, and related reagents is of preparative value. The third and most important stimulus which led to the investigation of these reactions has been the endeavour to understand their mechanism.

This review surveys and gives a systematic account of the available data and puts forward considerations concerning certain details of the mechanism of the oxidative substitution of the halogens at a saturated carbon atom.

II. REACTIONS OF ALKYLIODIDES AND BROMIDES WITH Cl_2, Br_2, AND ICl

In the last century, it was already known that alkyl iodides and t-alkyl bromides interact under mild conditions (at a low temperature in inert solvents) with molecular chlorine to form alkyl chlorides and I_2 or Br_2.[1-3] In the 1950's, this unusual substitution reaction at a saturated carbon atom attracted the attention of theoretical chemists.

Like aryl iodides, on chlorination alkyl iodides afford organic compounds of tervalent iodine, which, however, are unstable and readily decompose to alkyl chlorides and molecular iodine:[4,5]

$$CH_3I + Cl_2 \xrightarrow{-196^\circ C} CH_3ICl_2 \xrightarrow{-30^\circ C} CH_3Cl + ICl .$$

The first data on the mechanism of these reactions were obtained as a result of the study of the kinetics of the reactions of ICl with alkyl iodides and bromides in CCl_4 at 25 °C.[6,7] For the reaction of benzyl bromide and iodide with ICl in the presence of a large excess of the benzyl halide, the rate equation was obtained:

$$\frac{d(IX)}{dt} = k[C_6H_5CH_2X][ICl]^2 .$$

The reaction of isopropyl iodide is also of second order with respect to ICl but the rate is not directly proportional to the concentration of isopropyl iodide; analogous data have been obtained also for t-butyl bromide. The reaction of t-butyl iodide with ICl is so fast that its rate cannot be investigated even in very dilute solutions.

Under the given conditions, benzyl halides give rise to the corresponding chlorides, while in the case of isopropyl iodides mainly chloroiodopropane is formed. In the reaction with t-butyl bromide, a complex mixture of dihalogenoisobutanes is formed together with t-butyl chloride:

$$(CH_3)_3CBr \xrightarrow{ICl} (CH_3)_3CCl + C_4H_8ICl + C_4H_8Cl_2 + C_4H_8BrCl\ .$$

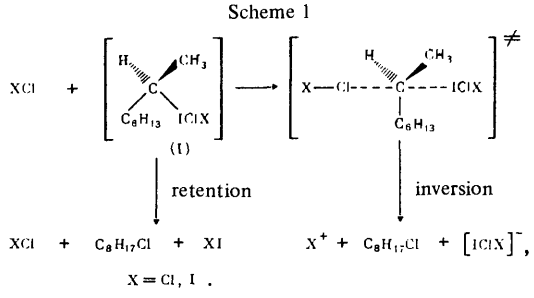
Kinetic data led to the conclusion that the rate-determining stage in the given reaction consists in the attack by the ICl molecule on the alkyl halide–iodine monochloride complex:

$$R{-}I \rightarrow I{-}Cl + ICl \rightarrow \text{products}.$$

The stereochemistry of the substitution of iodine by chlorine and bromine has been investigated in relation to the optically active 2-iodo-octane.[8,9] The reaction of 2-iodo-octane with Cl_2, ICl, and Br_2 proceeds smoothly at −78–0 °C in inert solvents (CH_2Cl_2, $CHCl_3$, CCl_4) and also in a mixture of CH_2Cl_2 with CH_3OH or pyridine, in the absence or presence of HCl, with formation of 2-chloro- and 2-bromo-octanes, preferentially with inversion of the configuration. The higher the polarity of the medium, the greater the amount of the product with inverted configuration formed. Thus the ratios c_i/c_r (c_i and c_r are the amount of products with the inverted and retained configurations respectively) in the reaction of optically active 2-iodo-octanes with an excess of Cl_2 in CH_2Cl_2 and 3:1 CH_2Cl_2–CH_3OH and [CH_2Cl_2–CH_3OH (3:1)]–HCl (4 M) mixtures are respectively 1.5, 5.8, and 10.2.[8] An analogous dependence of c_i/c_r on the polarity of the medium has been observed for the reaction of 2-iodo-octanes with ICl.

According to Corey and Wichter,[8] the results agree with a mechanism involving bimolecular nucleophilic substitution of the complex of alkyl iodide with the halogen (I) by a halogen molecule in accordance with Scheme 1:

Scheme 1



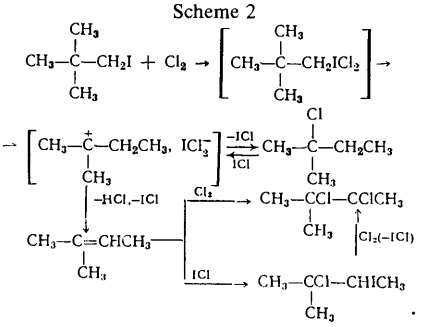
Attack on the complex (I) by the external nucleophile XCl leads to inversion of configuration, while intramolecular capture of chlorine in the complex (I) leads to the retention of configuration of the alkyl chloride. The complex (I) is in essence an intermediate—an organic compound of tervalent iodine. The mechanism presupposing the heterolysis of the complex (I) to the 2-octylcarbonium ion (II) is unlikely:

$$\underset{(I)}{[C_8H_{17}ICIX]} \rightarrow \underset{(II)}{[C_8H_{17}]^+} + [ICIX]^- \rightarrow C_8H_{17}Cl + IX\ .$$

In this mechanism, one would have to expect a higher degree of racemisation of 2-octyl chloride on increase in the polarity of the reaction medium.

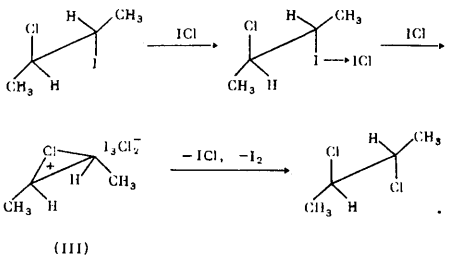
The reaction of neopentyl iodide with molecular iodine yielded t-pentyl chloride and 2,3-dichloro-2-methylbutane.[9] Special experiments showed that t-pentyl chloride also gives rise to 2,3-dichloro-2-methylbutane on treatment with a mixture of ICl and Cl_2, while the reaction with pure Cl_2 does not occur. A mechanism of the reaction of neopentyl chloride with Cl_2 has been proposed on the basis of the data obtained:[9]

Scheme 2



The kinetics and stereochemistry of the reactions of vicinal chloroiodoalkanes with ICl in CCl_4, leading to vicinal dichlorides, have been investigated in a recent study.[10] The reaction of 3-chloro-2-iodo-2,3-dimethylbutane with ICl has overall third order—first with respect to the substrate and second with respect to ICl. The substitution of iodine in *erythro*- and *threo*-3-chloro-2-iodobutanes takes place stereospecifically with retention of configuration, which can be explained by the involvement of the vicinal chlorine in retention of the configuration of the carbonium ion intermediate (III).

Scheme 3



The reactions of *erythro*- and *threo*-2-chloro-1-iodo-1-phenylpropanes with ICl proceed non-stereospecifically and in each case lead to a mixture of *erythro*- and *threo*-1,2-dichloro-1-phenylpropanes. This result can be explained by the fact that the geminal phenyl substituent delocalises the positive charge on the carbonium ion intermediate and thereby prevents the involvement of the neighbouring chlorine in the formation of the bridged cation of type (III).

A single example of the use of iodine trichloride in oxidative substitution reactions has been described in the literature.[11] When n-pentyl iodide reactions with ICl_3 in CH_2Cl_2, n-pentyl chloride is formed in a high yield.

III. REACTIONS OF ALKYL HALIDES WITH NITRIC ACID AND OTHER INORGANIC OXIDANTS

It was observed in 1968 that, when αβ-dibromo-α-nitroalkanes (IV) are treated with concentrated nitric acid at 40–50 °C, the bromide atom in the β-position is replaced by the nitrate group with liberation of elemental bromine in accordance with the scheme[12]

$$2O_2NCBrCBr + 4HNO_3 \rightarrow 2O_2NCBrCONO_2 + Br_2 + N_2O_4 + 2H_2O .$$

(IV) (V)

The bromine atom in the α-position is not substituted by the nitrate group. The corresponding nitric acid esters (V) have been isolated in 35–75% yields. The authors investigated this unusual reaction in detail.[13,14] It was established that alkyl iodies interact most readily (at temperature below 0 °C) with nitric acid. The reactivity of alkyl iodides varies in the sequence tertiary > secondary > primary. Under these conditions, the chlorine and bromine atoms in the molecule are not substituted, for example:

$$CH_3CHICH_2Br \xrightarrow[-5-0°C]{98\%HNO_3} CH_3CHCH_2Br \quad 46\%$$
$$\qquad\qquad\qquad\qquad\qquad\quad ONO_2 ,$$
$$CH_2ClCHICH_2Cl \xrightarrow[-3-0°C]{98\%HNO_3} CH_2ClCHCH_2Cl \quad 53\%$$
$$\qquad\qquad\qquad\qquad\qquad\quad ONO_2 .$$

Alkyl bromides react with nitric acid with greater difficulty than alkyl iodides. The corresponding nitrates are obtained from secondary alkyl bromides at 10–15 °C in yields up to 80%. Primary alkyl bromides react with still greater difficulty and at higher temperatures. The reaction is accompanied by the oxidative decomposition of the nitrate and the yield of the nitrolysis product is therefore reduced:

$$CH_2ClCH_2Br \xrightarrow[0-20°C]{HNO_3-H_2SO_4} CH_2ClCH_2ONO_2 \quad 31\% .$$

Iodocarboxylic acids and their esters also react with nitric acid to form the corresponding nitrates:[14]

$$ICH_2CO_2H \xrightarrow[0-4°C]{HNO_3-(CH_3CO)_2O} O_2NOCH_2CO_2H \quad 46\% ,$$
$$CH_3CHICO_2CH(CH_3)_2 \xrightarrow[12-16°C]{HNO_3} CH_3CHCO_2CH(CH_3)_2 \quad 70\% .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad ONO_2$$

The nitrolysis of the optically active 2-iodo-, 2-bromo-, and 2-chloro-octanes with nitric acid or a mixture of nitric acid and acetic anhydride affords the optically inactive 2-octyl nitrate. On this basis, it has been concluded[13] that the reaction proceeds with formation of carbonium ion intermediates. This is confirmed by the finding that elimination products (alkenes) are formed in the nitrolysis of t-butyl chloride and 2-bromo-octane, which subsequently give rise to addition products:

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow[-Cl_2]{HNO_3} \left[CH_3-\overset{CH_3}{\underset{+}{C}}-CH_3\right] \xrightarrow[-H^+]{} \left[CH_2=\overset{CH_3}{C}-CH_3\right] \xrightarrow{HNO_3} CH_2(NO_2)-\overset{CH_3}{\underset{ONO_2}{C}}(CH_3) ,$$

$$C_6H_{13}CHBrCH_3 \xrightarrow[-Br_2]{HNO_3} [C_5H_{11}\overset{+}{C}HCH_3] \xrightarrow[-H^+]{HNO_3} C_6H_{13}CHCH_3 ,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad ONO_2$$
$$[C_5H_{11}CH=CHCH_3] \xrightarrow{Br_2} C_5H_{11}CHBrCHBrCH_3 .$$

Further study of the interaction of iodo- and bromo-alkanes with nitric acid, nitrogen pentoxide, acetyl nitrate, and nitryl chloride shows that the active species inducing the heterolytic dissociation of the covalent carbon–halogen bond in the organic halogeno-derivative is the nitronium cation:[15]

Scheme 4

$$NO_2X \rightleftarrows NO_2^+ + X^- , \qquad (6)$$

$$RHal + NO_2^+ \rightleftarrows R^+ + NO_2Hal \rightarrow NO_2 + {}^1/_2Hal_2 , \qquad (7)$$

$$R^+ + X^- \mapsto RX \qquad (8)$$

X=ONO_2, CH_3COO, Cl; Hal=I, Br.

The necessary condition in the oxidative substitution of halogeno-alkanes is the oxidation of the eliminated halogen to Hal_2 [reaction (7)], which shifts the reaction equilibrium towards the formation of the carbonium ion. The primary carbonium ions formed undergo a rearrangement which results in the formation of a mixture of isomeric substitution products. Thus the interaction of 1-iodopropane with 98% HNO_3 in CH_2Cl_2 at −18 – −20 °C results in the formation of a a 48.6 : 51.4 mixture of 1-propyl and 2-propyl nitrates, while several products were obtained from 1-iodo-octane under these conditions: 1-octyl nitrate, 2-octyl nitrate, and 3(4)-octyl nitrate in proportions of 23.2 : 29.2 : 47.6. The authors note that the isomeric composition of the reaction products depends on many factors: the order in which the reactants are mixed, the concentration of nitric acid, the reaction temperature, etc. For example, when a solution of 1-iodo-butane in methylene chloride is added to nitric acid (in molar proportions of 1 : 10), the ratio of 1- and 2-butyl nitrates is 18 : 82, while for the reverse order of the addition the ratio is 96 : 4.

Treatment of 1-bromobutane with a mixture of concentrated nitric acid and acetic anhydride at 15–20 °C leads to the formation of 1-butyl nitrate (15.7%), 2-butyl nitrate (63.0%), 1-butyl acetate (8.1%), and 2-butyl acetate (13.2%).

Not only nitric acid but also HCl, HBr, or HF can act as nucleophiles in the oxidative substitution of the halogens in organic halogeno-derivatives.[16-18] H_2O_2, $KMnO_4$, $K_2Cr_2O_7$, $KClO_3$, $NaNO_2$, and chlorinated lime can also act as oxidants together with HNO_3:[17]

$$RI \xrightarrow{\text{oxidant}} [R^+] \xrightarrow{HCl} RCl ,$$
$$\qquad\qquad\qquad\quad \xrightarrow{HBr} RBr ,$$
$$RI\,(Br) \xrightarrow{HNO_3} [R^+] \xrightarrow{HF} RF .$$

When HCl is passed into a mixture of iodoalkanes with hydrogen peroxide, the yield of the corresponding chloroalkanes reaches 88%. $KMnO_4$ and $K_2Cr_2O_7$ are active oxidants: the reactions in their presence are carried out with slight heating and the yield of chloro-alkanes exceeds 90%. When 2-iodo- or 2-bromo-alkanes are treated with a mixture of concentrated nitric acid and anhydrous hydrogen fluoride, the yield of 2-fluoroalkanes exceeds 70%.

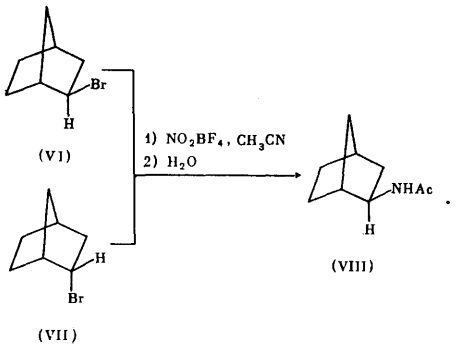
The reactions of alkyl halides with nitronium and nitrosonium fluoroborates in acetonitrile, leading to substituted acetamides, are also a type of oxidative substitution:[19-22]

$$R_3CX + NO_2BF_4 \xrightarrow{-NO_2X} [R_3C^+] \xrightarrow{CH_3CN} [R_3C\overset{+}{N}\equiv CCH_3] \xrightarrow{H_2O} R_3CNHAc .$$

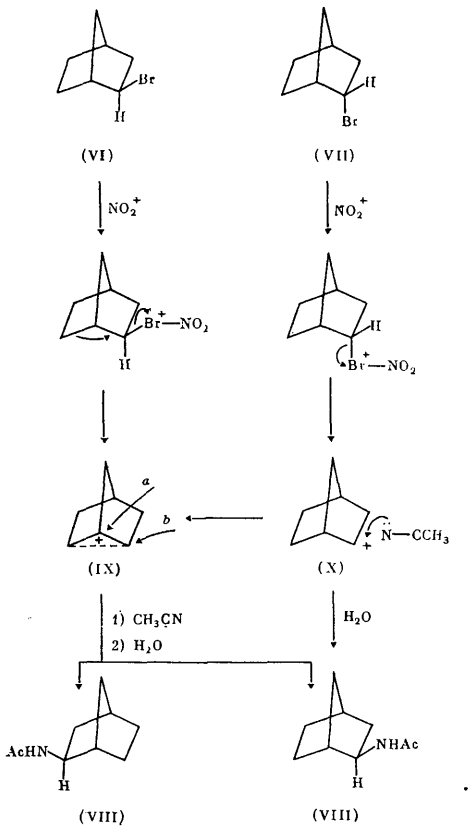
X=I, Br, Cl, F

The reactivity of alkyl derivatives varies in the sequence RI > RBr ≫ RCl > RF. In the general case, the ease of elimination of X corresponds to the stability of the carbenium ions: tertiary > secondary > primary. The relative reactivities of adamantane derivatives are AdF : AdCl : AdBr : AdI = 1 : 6.6 : 67 : 240.[21]

The oxidation of the optically active *exo*-2-norbornyl bromide (VI) under these conditions affords the optically inactive *N*-(exo-2-norbornyl)acetamide (VIII) whilst the optically active *endo*-isomer (VII) gives rise to the *exo*-acetamide (VIII) having a low optical activity (1.2–1.6%):[19]



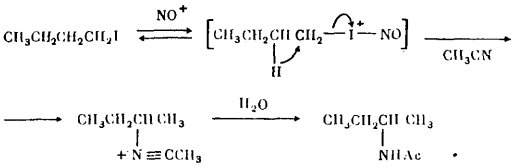
The heterolysis of the C—Br bond in *exo*-2-norbornyl bromide (VI) by the nitronium cation is accompanied by the nucleophilic attack on the C(2) atom by the electrons of the C(6)—C(1) bond, which results in the formation of the symmetrical non-classical bridged cation (IX). The capture of this cation by the solvent and the hydrolysis of the nitrylium ion afford the racemic *exo*-acetamide (VIII). In the case of the *endo*-isomer (VII), the involvement of the C(6)—C(1) bond in the heterolytic process is ruled out for geometrical reasons. The 2-norbornyl cation (X) formed is either captured by the solvent on the side opposite to that of the leaving group, or leads to the optically active *exo*-acetamide, or, to a much greater extent, rearranges to the bridge ion (IX), which gives rise to the *exo*-racemate (VIII).



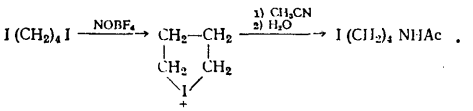
An analogous result has been obtained in the solvolysis of the optically active *exo*- and *endo*-2-norbornyl *p*-bromotoluenesulphonates.[23] In the case of the optically active *endo*-*p*-bromotoluenesulphonate, 7—8% of the optical activity was retained, while the *exo*-isomer yielded only the *exo*-racemate.

The substitution of bromine in the optically active 2-bromooctane on treatment with nitronium fluoroborate in acetonitrile takes place preferentially with inversion of configuration.[19]

Nitrosonium fluoroborate is somewhat less reactive in the oxidative substitution reaction than nitronium fluoroborate.[22] Tertiary and secondary alkyl iodides react smoothly with $NOBF_4$ in acetonitrile at 0 °C with formation of the corresponding amides. The primary iodides react more smoothly and afford a mixture of 1-alkyl- and 2-alkyl-amides:



A rearrangement is not observed for 1,4-diiodobutane owing to the involvement of iodine in the formation of a five-membered iodonium intermediate:



IV. REACTIONS OF ALKYL IODIDES WITH ORGANIC PEROXY-ACIDS

The oxidative substitution of iodine in alkyl iodides when the latter are treated with organic peroxy-acids has been thoroughly investigated[24–30] and it has been established[25] that the complete oxidation of one mole of n-heptyl iodide in methylene chloride requires about two moles of *m*-chloroperoxybenzoic acid. The products of the initial state of this reaction are O_2, I_2, and I_2O_5. The overall stoichiometry of the reaction is described by the set of equations

$$6ArCO_3H + 6RI \rightarrow 6[R\overset{+}{I}\overline{O}] + 6ArCO_2H,$$
$$6[R\overset{+}{I}\overline{O}] + 6H_2O \rightarrow 6ROH + 6HOI,$$
$$6HOI \rightarrow 4HI + 2HIO_3,$$
$$4HI + 2ArCO_3H \rightarrow 2ArCO_2H + 2I_2 + 2H_2O,$$
$$2HIO_3 \rightarrow I_2O_5 + H_2O,$$
$$n\,ArCO_3H \xrightarrow{[cat.]} n\,ArCO_2H + (n/2)\,O_2;$$
$$(8+n)\,ArCO_3H + 6RI + 3H_2O \rightarrow (8+n)\,ArCO_2H + 6ROH + 2I_2 + I_2O_5 + (n/2)\,O_2.$$

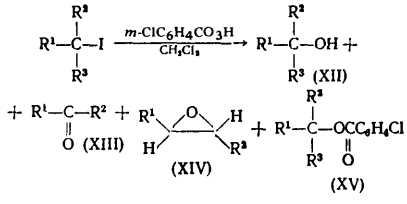
$R = n\text{-}C_7H_{15}$, $Ar = m\text{-}ClC_6H_4$, $n = 4\text{-}16$.

The iodoso-group in the intermediate iodo-compound $R\overset{+}{I}\overline{O}$ is substituted in this case by water, which is present in the peroxy-acid as an impurity. Careful drying of *m*-chloroperoxybenzoic acid and of the solvent reduces the amount of alcohol (60%) and increases that of n-heptyl *m*-chlorobenzoate (40%). This ratio is close to the maximum possible, because 0.5 mole of water is formed on oxidation of one mole of alkyl iodide. When the water-saturated solvent is used, the alcohol is formed exclusively.

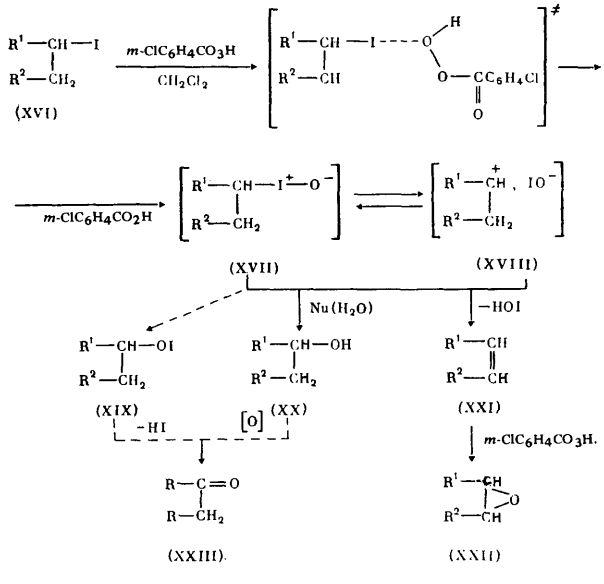
The reactivity of alkyl iodides in relation to organic peroxy-acids varies in the sequence tertiary > secondary > primary. The character of the products formed on oxidation of alkyl iodides is determined by the type of substrate and solvent. When a non-nucleophilic solvent (CH_2Cl_2, C_6H_6) or a solvent with a low nucleophilic activity [tetrahydrofuran (THF), $(C_2H_5)_2O$, C_2H_5OAc] is used, the primary alkyl iodides give rise to the corresponding alcohols and *m*-chlorobenzoates. Secondary and tertiary alkyl iodides, afford, together with substitution products, also carbonyl compounds and epoxides. By carrying out this reaction over a wide temperature range (from -80 to 80 °C), it has been shown that it leads to the same products and only their ratio depends on the temperature.

The dependence of the composition of the products on the type of substrate (in accordance with Scheme 5) is indicated in the Table.

Scheme 5

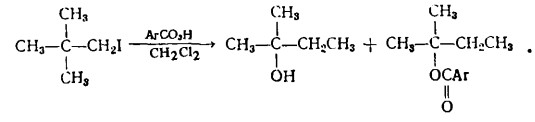


The authors explain the formation of the observed products in the following way:



The alkyl iodide (XVI) is oxidised by *m*-chloroperoxybenzoic acid to the iodoso-compound (XVII), which can dissociate to the ion pair (XVIII). The rearrangement of the iodoso-compound (XVII) to the hypoiodite (XIX) probably proceeds via the ion pair (XVIII). Nucleophilic attack on the iodoso-compound or the ion pair leads to the formation of the substitution products (XX). The elimination of HOI from the iodoso-compound (XVII) results in the formation of the alkene (XXI), which is oxidised under the reaction conditions to the epoxide (XXII). The ketone (XXIII) is formed as a result of the oxidation of the alcohol (XX) and also probably on elimination of HI from the intermediate alkyl hypoiodite (XIX).

Carbonium ion rearrangements on interaction of alkyl iodides with peroxy-acids are observed only when the substitution of iodine is sterically hindered. Thus t-pentyl alcohol and the corresponding *m*-chlorobenzoate have been obtained in the reactions involving neopentyl iodide:

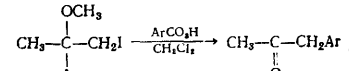


The results of the reactions of alkyl iodides $R^1R^2R^3CI$ with *m*-chloroperoxybenzoic acid.[25]

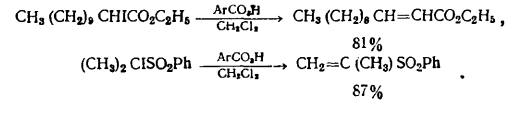
R^1	R^2	R^3	Solvent	*t*° C	Product ratios			
					(XII)	(XIII)	(XIV)	(XV)
n-C_6H_{13}	H	H	CH_2Cl_2	27	90	0	0	10
n-C_5H_{11}	CH_3	H	CH_2Cl_2	27	48	23	20	9
n-C_5H_{11}	CH_3	H	CH_2Cl_2	−80	55	18	23	4
n-C_5H_{11}	CH_3	H	C_6H_6	80	28	22	28	22
n-C_5H_{11}	CH_3	H	C_2H_5OAc	0	65	7	26	2
CH_3	CH_3	CH_3	CH_2Cl_2	27	85*	0	0	15*

*In all the experiments with the exception of the reaction with t-butyl iodide, the overall yield of the products was 80–100% for the total conversion of the initial compound: in the case of t-butyl iodide, the yield of the substitution product was 60%, the remaining 40% comprising low-boiling olefins and epoxides.

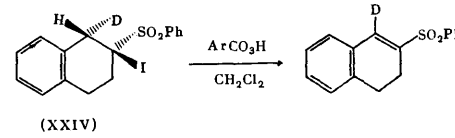
An analogous rearrangement has been observed[26] in the reaction of 2-aryl-1-iodo-2-methoxypropanes with *m*-chloroperoxybenzoic acid:



The elimination of HI can become the main reaction pathway in the presence of electronegative substituents at the α-carbon atom.[27] For example, the oxidation of ethyl 2-iododecanoate and 2-iodo-2-benzenesulphonylpropane with *m*-chloroperoxybenzoic acid leads to unsaturated compounds in a high yield:



It has been shown in relation to the bicyclic iodide (XXIV) that alkenes are formed as a result of *syn*-elimination:



(XXIV)

The quantitative formation of 1,2-epoxycyclohexane in the oxidation of cyclohexyl iodide by *m*-$ClC_6H_4CO_3H$ in methylene chloride has been noted.[28]

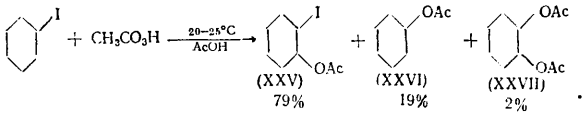
The oxidation of alkyl iodides in nucleophilic solvents (CH_3OH, CH_3COOH) gives rise mainly to products involving the solvent:[28-30]

$$CH_3(CH_2)_6CH_2I \xrightarrow[CH_3OH]{ArCO_3H} CH_3(CH_2)_6CH_2OCH_3\ ,\quad 91\%$$

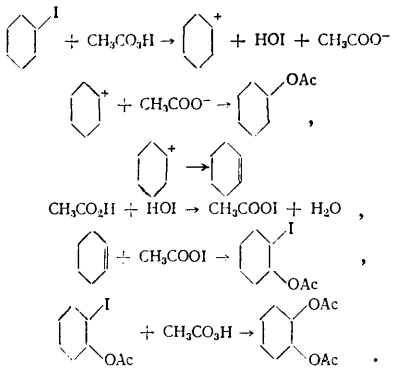
$$CH_3(CH_2)_6CHICH_3 \xrightarrow[AcOH]{ArCO_3H} CH_3(CH_2)_5\underset{\displaystyle OAc}{\underset{|}{C}}HCH_3 + CH_3(CH_2)_6\overset{\displaystyle O}{\overset{\|}{C}}CH_3\ .$$

84% 15%

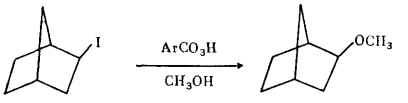
The oxidation of cyclohexyl iodide by peroxyacetic acid in acetic acid produces, in contrast to the reaction with *m*-$ClC_6H_4CO_3H$ in CH_2Cl_2, the vicinal iodoacetate (XXV) together with cyclohexyl acetate (XXVI) and diacetate (XXVII).[29] For a reactant : substrate ratio of 0.7, the following proportions of the products have been obtained:



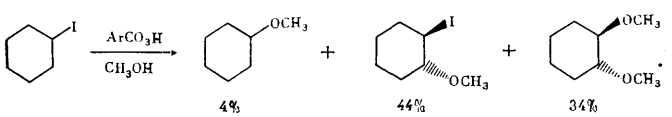
With increase in the peroxyacetic : cyclohexyl iodide ratio, the amount of iodoacetate (XXV) diminishes and that of the diacetate (XXVII) increases. The authors proposed the following reaction scheme:



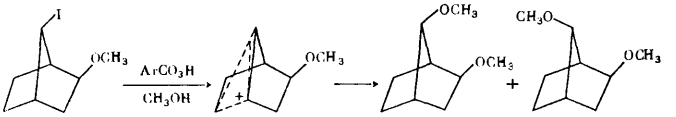
The reactions of alkyl iodides with *m*-chloroperoxybenzoic acid in methanol,[6] in which the corresponding methyl ethers have been obtained in high yield in most cases, have been studied in detail:[30]



The interaction of cyclohexyl iodide with two equivalents of *m*-chloroperoxybenzoic acid led to the isolation of products analogous to those obtained in the reaction with peroxyacetic acid in acetic acid:



Under the given conditions, it has been possible to substitute iodine in highly inert systems such as 1- and 7-bicyclo[2.2.1]heptyl iodides, but, compared with other substrates, under these conditions a (7 – 10)-fold excess of oxidant is necessary. The formation of products with the preferential retention of configuration in the oxidative substitution of iodine in the 7-*syn*-iodide (XXVIII) is explained by the fact that the intermediate species is the σ-delocalised 7-bicyclo-[2.2.1]heptyl cation (XXIX):



(XXVIII) (XXIX) 66% 15%

The influence of various lithium salts on the character of the oxidative substitution product has been investigated in relation to the reaction of n-octyl iodide with *m*-chloroperoxybenzoic acid. It was found that, in the presence of a five-fold excess of lithium chloride or bromide, the main reaction products become the corresponding chlorides and bromides, but the addition of lithium fluoride and perchlorate does not result in the formation of "participation products":

$$CH_3(CH_2)_6CH_2I \xrightarrow[CH_3OH,LiX]{ArCO_3H} CH_3(CH_2)_6CH_2X + CH_3(CH_2)_6CH_2OCH_3\ ;$$

70–80% 10–15%

X = Cl, Br .

The stereochemistry of the oxidative substitution of iodine by peroxy-acids has been investigated in relation to the optically active 2-iodo-octane.[28,30] The substitution of iodine in (*S*)(+)-2-iodo-octane in methylene chloride affords a mixture of products containing (*R*)(–)-octan-2-ol 56%, the corresponding *m*-chlorobenzoate (29%), octan-2-one (9%), as well as traces of octan-3-ol. Thus the chiral reaction products are formed with complete inversion of configuration, which indicates the operation of the S_N2 mechanism. However, when the reaction is carried out in methanol,[30] the corresponding methyl 2-octyl ether is formed only with the preferential inversion of configuration (c_i/c_r = 2), which indicates the partial heterolysis of the intermediate iodoso-compound on passing to a more polar solvent.

The iodoso-group is an excellent leaving group, comparable in its ability to be substituted to the diazo-group in alkanediazonium ions. It is well known that the solvolysis of the aryl ethers of β-phenylethanol in aqueous and alcoholic media proceeds without a rearrangement,[31] but the oxidation of the deuterium-labelled 1-iodo-2-phenylethane in methylene chloride results in the formation of 35% of the alcohol with migration of the phenyl group. Similarly the deamination of labelled β-phenylethylamine in aqueous solution yields 27% of the alcohol with a displaced phenyl group:[32]

$$PhCH_2CD_2I \xrightarrow[CH_2Cl_2]{ArCO_3H} PhCH_2CD_2OH + PhCD_2CH_2OH\ ,$$

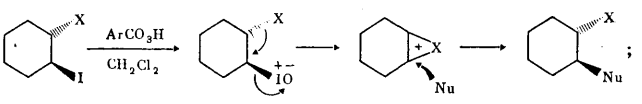
65% 35%

$$Ph^{14}CH_2CH_2NH_2 \xrightarrow[H_2O]{HNO_2} Ph^{14}CH_2CH_2N_2^+OH^- \rightarrow$$

$$\rightarrow Ph^{14}CH_2CH_2OH + PhCH_2^{14}CH_2OH\ .$$

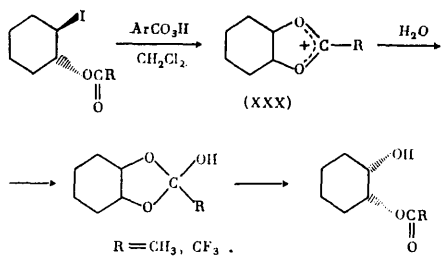
73% 27%

The substitution of iodine in *trans*-vicinally substituted iodocyclohexanes affords alcohols and the corresponding *m*-chlorobenzoates with retention of configuration also as a result of the involvement of the neighbouring group:



X = Cl, Br, OH, OCH_3, N_3 .

The formation of *cis*-hydroxyethers from *trans*-2-iodocyclohexyl acetate or trifluoroacetate is explained by the attack of water on the C(2) atom in the 2-alkyl-1,3-dioxolanolium ion (XXX).



(XXX)

Analogous results have been obtained in the oxidation of *trans*-vicinally substituted iodocyclohexanes by iodine trifluoroacetate (III).[33,34] The reaction with *trans*-2-bromo-1-iodocyclohexane yielded a product with retention of configuration, while in the reaction with 2-iodocyclohexyl trifluoroacetate the configuration is inverted.

V. INTERACTION OF ALKYL HALIDES WITH HYPOHALITE DERIVATIVES OF STRONG ACIDS

Hypohalite derivatives of strong acids (fluorosulphonic, trifluoromethanesulphonic, perchloric, and nitric) have been synthesised and investigated comparatively recently.[35] These compounds are very strong electrophiles capable of substituting the halogen atoms in polyhalogenoalkanes by the strong acid residue.

The hypohalite derivatives of fluorosulphonic acid, usually referred to as halogen fluorosulphates, have been most thoroughly investigated among compounds of this class.[36–48] Chlorine and bromide fluorosulphates readily interact even at temperatures below 0 °C with usually inert solvents such as CH_2Cl_2, CCl_4, and $CHCl_2CHCl_2$:[38–38]

$$CH_2Cl_2 + ClOSO_2F \xrightarrow{<0^\circ C} CH_2ClOSO_2F + Cl_2 ;$$
$$CCl_4 + n\,BrOSO_2F \xrightarrow{-22^\circ C} CCl_{4-n}(OSO_2F)_n + n\,BrCl ;$$
$$n = 1-4 .$$

Owing to the high reactivity of halogen fluorosulphates and also the low stability of the non-halogenated alkyl fluorosulphates,[38,47] these reagents have been investigated in reactions with polyfluoroalkyl halides. The reactivity of perfluoroalkyl halides in relation to chlorine fluorosulphate varies in the sequence $R_FI > R_FBr > R_FCl$.[35,39] Thus, perfluoroalkyl iodides are converted into solid white or cream coloured compounds, probably having the structure $R_FI(OSO_2F)_2$, already at tempereatures between −50° and −40 °C. With increase in temperature, these compounds decompose into perfluoroalkyl fluorosulphates and iodine fluorosulphates:[40]

$$R_FI + ClOSO_2F \xrightarrow{-50^\circ C} [R_FICIOSO_2F] \xrightarrow{ClOSO_2F} \rightarrow R_FI(OSO_2F)_2 \xrightarrow{-20^\circ C} R_FOSO_2F + IOSO_2F$$
$$R_F = CF_3,\ n\text{-}C_3F_7,\ n\text{-}C_7F_{15}.$$

Perfluoroalkyl bromides react with chlorine fluorosulphate under more severe conditions. Both primary bromine atoms in 1,2-dibromoperfluoroethane and 1,3-dibromoperfluoropropane can be substituted only at 50–60 °C:[40]

$$Br(CF_2)_3Br + ClOSO_2F \xrightarrow[48\ h]{65^\circ C} \underset{64\%}{FSO_2O(CF_2)_3OSO_2F} + \underset{31\%}{Cl(CF_2)_2OSO_2F} .$$

The secondary bromine atoms are not involved under these conditions. The chlorine atoms in chlorofluoroalkanes are substituted with even greater difficulty. The reaction is catalysed by fluorosulphonic acid.[41–43] Thus Freon 112 ($CFCl_2CFCl_2$) does not react with chlorine fluorosulphate even after prolonged heating (at 70–80 °C), but, after the addition of catalytic amounts of FSO_3H (5 mole %) an exothermic reaction begins at room temperature and is completed after 5 h at 35–45 °C:[41]

$$CFCl_2CFCl_2 + ClOSO_2F \xrightarrow{35-45^\circ C} CFCl_2CFClOSO_2F .$$

Freon 112 (CF_2Cl_2) reacts similarly but 1,2-dichlorohexafluoropropane does not react even at 100 °C.

In the presence of catalytic amounts of FSO_3H, chlorine fluorosulphate interacts with Freon 113 ($CF_2ClCFCl_2$) at 40–50 °C, but the completion of the reaction requires 8 h. The catalytic action of fluorosulphonic acid probably consists in protonating the $ClOSO_2F$ molecule, as a result of which the partial positive charge on the chlorine atom increases:[36,42]

$$ClOSO_2F + HOSO_2F \rightleftarrows \overset{+}{Cl}(H)-O-SO_2F + OSO_2F^- .$$

In fluorosulphonic acid at room temperature, chlorine fluorosulphate substitutes one chlorine atom and at 85 °C a second chlorine atom in Freon 113; all three chlorine atoms are substituted in a superacid medium (HSO_3F/SbF_5):

$$CF_2ClCFCl_2 + ClOSO_2F \xrightarrow[40-50^\circ C]{cat.\ HSO_3F} \underset{84\%}{CF_2ClCFClOSO_2F} ,$$
$$CF_2ClCFCl_2 + ClOSO_2F \xrightarrow[\sim 20^\circ C]{HSO_3F} CF_2ClCFClOSO_2F \xrightarrow{65^\circ C} \underset{65\%}{CF_2ClCF(OSO_2F)_2}$$
$$CF_2ClCFCl_2 + ClOSO_2F \xrightarrow[30^\circ C]{HSO_3F/SbF_5} FSO_2OCF_2CF(OSO_2F)_2 \rightarrow$$
$$\xrightarrow{HSO_3F/SbF_5} FSO_2OCF_2C(=O)F + S_2O_6F_2$$
$$\sim 50\% \qquad \sim 50\% .$$

With the aid of chlorine fluorosulphate in the superacid medium, it has been possible to substitute the secondary bromine atom in 2-bromohexafluoropropyl fluorosulphate (XXXI):

$$\underset{(XXXI)}{CF_3CFBrCF_2OSO_2F} + ClOSO_2F \xrightarrow[80-100^\circ C]{HSO_3F/SbF_5} CF_3\underset{\displaystyle OSO_2F}{\underset{|}{C}}FCF_2OSO_2F .$$

However, even under these conditions the secondary chlorine and tertiary bromine atom in polyfluoroalkanes cannot be substituted.[43] The reactivity of chlorine fluorosulphate increases also after the addition of bromine, which has been explained by the formation of $BrOSO_2F$ *in situ*.[40] However, in a later study[43] it was shown that bromine fluorosulphate is less reactive than chlorine fluorosulphate; in particular, it reacts with compound (XXXI) in the superacid medium even at 120–130 °C. The catalytic action of bromine in reactions involving substitution by chlorine fluorosulphate has been explained[43,44] by the formation of the compound $BrCl(OSO_2F)_2$ as a possible intermediate, whose molecule contains a tervalent bromine atom. The same workers showed that bromine tris(fluorosulphate), which readily interacts with Freon 113, is even more reactive than chlorine fluorosulphate:[45]

$$CF_2ClCFCl_2 + Br(OSO_2F)_3 \xrightarrow[2\ h]{30^\circ C} \underset{51\%}{CF_2ClCFClOSO_2F} + \underset{39\%}{CF_2ClCF(OSO_2F)_2} .$$

In the superacid medium, $Br(OSO_2F)_3$ substitutes the chlorine atom in 2,3-dichloro-2-trichloromethyl pentafluoropropane.[44]

Iodine tris(fluorosulphate)† and iodine fluorosulphate do not substitute chlorine atoms in Freons in the presence of fluorosulphonic acid even on prolonged heating.[46] $I(OSO_2F)_3$ is capable of substituting only iodine by the fluorosulphate group in perfluoroalkyl iodides:[46]

$$n\text{-}C_3F_7I + I(OSO_2F)_3 \xrightarrow[120\ h]{20^\circ C} n\text{-}C_3F_7OSO_2F + I_3SO_2F + IOSO_2F\ .$$

Nevertheless iodine tris(fluorosulphate) and iodine fluorosulphate readily interact with ethyl chloride at room temperature:[46]

$$CH_3CH_2Cl \xrightarrow[-\frac{1}{3}ICl_3,\ -ICl]{\frac{1}{3}I(OSO_2F)_3,\ IOSO_2F} CH_3CH_2OSO_2F\ (50\%)\ .$$

As regards the mechanism of the interaction of halogen fluorosulphates with alkyl halides, it has been recently suggested[48] that, in the substitution of a halogen by the fluorosulphate group, the substituted halogen is initially oxidised to the tervalent state and the resulting intermediate (XXXII) decomposes under these conditions in accordance with the scheme

$$RHal + XOSO_2F \longrightarrow \underset{\text{(XXXII)}}{R(Hal)(X)(OSO_2F)} \longrightarrow ROSO_2F + HalX\ ;$$

$Hal = Cl, Br, I$; $X = Cl, Br, I, Br(OSO_2F)_2, I(OSO_2F)_2$.

The proposed scheme is hardly applicable to the substitution of chlorine atoms in alkyl halides by bromine and iodine fluorosulphates. In particular, it is unlikely that the electropositive iodine should oxidise the chlorine atom in C_2H_5Cl to the tervalent state in the above reaction of ethyl chloride with $I(OSO_2F)_3$ or $IOSO_2F$.

Chlorine and bromine trifluoromethanesulphonates are also capable of substituting the Cl and Br atoms in perfluorohalogenoalkanes by the trifluoromethanesulphonate group. In contrast to the analogous fluorosulphates, chlorine and bromine trifluoromethanesulphonates are unstable at temperatures above 0 °C and the reactions with them have therefore been carried at low temperatures (down to −160 °C).[49] Comparison of the reactivities of chlorine and bromine trifluoromethanesulphonates and fluorosulphates shows readily that the corresponding trifluoromethanesulphonates are significantly more vigorous reagents. For example, the reaction of $ClOSO_2CF_3$ with Freon 12 takes place readily at −60 °C,[50,51] while in the case of chlorine fluorosulphate heating to 80 °C is necessary:[41]

$$CF_2Cl_2 + ClOSO_2CF_3 \xrightarrow{-60^\circ C} CF_2ClOSO_2CF_3\ ,$$
$$CF_2Cl_2 + ClOSO_2F \xrightarrow{80^\circ C} CF_2ClOSO_2F\ .$$

As for chlorine and bromine fluorosulphates, the reactivity of $ClOSO_2CF_3$ is higher than that of $BrOSO_2CF_3$, which can be seen especially well in the reactions with perfluoroalkyl bromides:[50]

† Bromine tris(fluorosulphate) and iodine tris(fluorosulphate) are considered in this Section as compounds related to the hydrophalite derivatives of fluorosulphonic acid.

$$CF_3Br + ClOSO_2CF_3 \xrightarrow[1\ h]{-111^\circ C} \underset{95\%}{CF_3OSOCF_3}\ ,$$
$$CF_3Br + BrOSO_2CF_3 \xrightarrow[15\ h]{-111\div-10^\circ C} \underset{58\%}{CF_3OSO_2CF_3}\ .$$

In relation to $ClOSO_2CF_3$, the reactivity of alkyl chlorides decreases in the sequence

$$CCl_4 > CCl_3F > CCl_2F_2 > CF_3Cl\ .$$

Chlorotrifluoromethane does not react with $ClOSO_2CF_3$ in the course of 24 h at temperatures in the range −111 − 22 °C. The reactivity series obtained can be accounted for by the decrease in the negative charge on the chlorine atom with increase in the number of fluorine atoms, which should hinder the interaction with the electropositive halogen in $ClOSO_2CF_3$. Under the conditions indicated, the secondary bromine atoms in perfluoroalkanes are not substituted, which the authors explain by the increasing steric hindrance.[50]

The stereochemistry of the substitution of the chlorine atom in *erythro*- and *threo*-$CF_3CO_2CHFCHFCl$ has been investigated.[50] For each diastereoisomer, one diastereoisomer of trifluoromethanesulphonate (XXXIII) was obtained:

$$CF_3CO_2CHFCHFCl + ClOSO_2CF_3 \xrightarrow{-111\div22^\circ C} \underset{\text{(XXXIII)}}{CF_3CO_2CHFCHFOSO_2CF_3}\ .$$

Careful examination of the ^{19}F NMR spectra of the diastereoisomers obtained enabled the authors to conclude that the substitution takes place with retention of configuration. On the basis of the data obtained, a synchronous cyclic mechanism of the type S_Ei was proposed:

Scheme 6

$$\equiv C{-}Cl + ClOSO_2CF_3 \longrightarrow \equiv C{-}Cl{\cdots}OSO_2CF_3 \longrightarrow \equiv C{-}OSO_2CF_3 + Cl_2\ .$$

The hypochlorite derivative of perchloric acid (chlorine perchlorate) and virtually all covalent perchlorates are explosive substances sensitive to impact. Chlorine perchlorate is itself stable at room temperature.[52] Perfluoroalkyl and perfluoroaryl iodides interact vigorously with chlorine perchlorate. As for the majority of the reactions of alkyl iodides with oxidants described above, here organic compounds of tervalent iodine (XXXIV) are formed initially and are then converted into the corresponding alkyl perchlorates (XXXV):[53]

$$2R_FI + 4ClOClO_3 \rightarrow \underset{\text{(XXXIV)}}{(R_F)_2I^+I(OClO_3)_4^-} \rightarrow \underset{\text{(XXXV)}}{2R_FOClO_3} + 2[IOClO_3]\ .$$

The intermediates (XXXIV) have been isolated and characterised for R_F = n-C_7F_{15}, iso-C_3F_7, or C_6F_5. The covalent perchlorates (XXXV) cannot always be obtained on heating the intermediates (XXXIV). Thus explosions occurred in the cases of the perfluorophenyl and perfluoroisopropyl derivatives.

Perfluoroalkyl bromides interact just as readily with chlorine perchlorate and afford covalent perchlorates in satisfactory yields. Molecular chlorine and bromine perchlorates are then produced:

$$R_FCFBrCF_2Br + ClOClO_3 \xrightarrow{-25\div0^\circ C} \underset{40-90\%}{R_FCFBrCF_2OClO_3} + BrOClO_3 + Cl_2\ .$$

Primary and secondary perfluoroalkyl chlorides do not enter into this reaction. In the less fluorinated chlorofluorohydrocarbons, the chlorine atoms can also be substituted:[53]

$$\begin{array}{l}CF_2{-}CCl_2\\ |\quad\ |\\ CF_2{-}CCl_2\end{array} + 2ClOClO_3 \rightarrow \begin{array}{l}CF_2{-}CClOClO_3\\ |\quad\ \ |\\ CF_2{-}CClOClO_3\end{array}.$$

Bromine perchlorate is formed in the reactions of $ClOClO_3$ with perfluoroalkyl bromides probably as a result of the oxidation of the elemental bromine formed as an intermediate; owing to the lower reactivity, $BrOClO_3$ accumulates in the reaction products:

$$R_FBr + ClOClO_3 \xrightarrow{k_1} R_FOClO_3 + BrCl,$$
$$BrCl \rightleftarrows {}^1/_2Br_2 + {}^1/_2Cl_2,$$
$${}^1/_2Br_2 + ClOClO_3 \xrightarrow{k_2} BrOClO_3 + {}^1/_2Cl_2.$$

The absence of appreciable amounts of elemental bromine may be evidence that Br_2 is oxidised more readily than the bromine atom in the perfluoroalkyl bromide, i.e. in the reaction schemes presented we have $k_2 > k_1$. Bearing in mind that chlorine trifluoromethanesulphonate[51] and chlorine fluorosulphate[54] readily oxidise Br_2 to the corresponding hypobromites, presumably an analogous picture obtains also in the substitution by these reagents of the bromine atoms in the relatively unreactive perfluoroalkyl bromides.

Yet another representative of reagents of this type, namely chlorine nitrate, is stable at low temperatures (–40 °C), decomposing gradually at 20–25 °C.[55] Trifluoromethyl iodide is readily oxidised at low temperatures by chlorine nitrate, but covalent alkyl nitrates have not been isolated, in contrast to the perchlorates:[56,57]

$$CF_3I + ClONO_2 \xrightarrow{-45^\circ C} [CF_3IClONO_2] \xrightarrow{-20^\circ C} CF_3I(ONO_2)_2 + Cl_2.$$

Trifluoromethyl iodosodinitrate decomposes at room temperature in accordance with the scheme[57]

$$10CF_3I(ONO_2)_2 \xrightarrow{20^\circ C} 5CF_3I + 5COF_2 + 10N_2O_4 + I_2 + IF_5 + I_2O_5.$$

VI. THE INTERACTION OF ALKYL HALIDES WITH HALOGEN FLUORIDES

The most readily available halogen fluorides, namely IF_5, BrF_3, ClF, and ClF_3, were tested as early as the 1930's–1950's as fluorinating agents in the substitutional fluorination reactions of polyhalogenohydrocarbons, mainly halogenomethanes:[58–61]

$$CHI_3 + IF_5 \rightarrow CHF_3 + I_2,$$
$$CBr_4 + BrF_3 \rightarrow CBrF_3 + Br_2,$$
$$CCl_4 + BrF_3 \rightarrow CCl_2F_2 + BrCl.$$

It was then already noted that, as the geminal halogen atoms (I, Br, Cl) are substituted by fluorine, further fluorination is hindered.

Bromine and chlorine trifluorides effectively substitute the iodine atoms by fluorine in perfluoroalkyl iodides, the corresponding perfluoroalkanes being then formed in high yields.[62] Later it was shown that at low temperatures the interaction of ClF_3 and BrF_3 with perfluoroalkyl iodides leads to the formation of the corresponding derivatives of tervalent and quinquevalent iodine:[63]

$$R_FI + 2ClF_3(BrF_3) \rightarrow R_FIF_2,$$
$$R_FI + 4ClF_3 \rightarrow R_FIF_4,$$
$$R_F = C_2F_5,\ C_4F_9,\ \text{etc.}$$

Overall, the early data surveyed in a number of reviews[59–61] led to the conclusion that halogen fluorides are relatively unselective reagents and that their application in organic chemistry would be restricted to reactions with highly halogenated substrates. Nevertheless, subsequent investigations demonstrated that highly reactive compounds such as ClF and BrF_3 can be used successfully for the selective substitution of bromine and chlorine atoms by fluorine in hydrogen-containing halogenoalkanes.[64–70] Thus the use of a solution of bromine trifluoride in bromine for the selective fluorination of bromofluoroethanes has been described:[64]

$$CF_3CHBr_2 \xrightarrow[25-35^\circ C]{BrF_3/Br_2} \underset{92\%}{CF_3CHBrF} + \underset{5\%}{CF_3CHF_2},$$
$$CF_2BrCH_2Br \xrightarrow{BrF_3/Br_2} \underset{77\%}{CF_3CH_2Br}.$$

A possible reaction mechanism taking into account the tendency of BrF_3 to undergo self-ionisation has been proposed:

$$2BrF_3 \rightleftarrows BrF_2BrF_4 \rightleftarrows BrF_2^+ + BrF_4^-,$$
$$-\overset{|}{C}-Br + BrF_2^+ \rightarrow [-\overset{|}{C}^{\delta+}\cdots Br\cdots Br^{\delta-}F_2] \rightarrow [-\overset{|}{C}^+] + [Br_2F_2],$$
$$[-\overset{|}{C}^+] + BrF_4^- \rightarrow -\overset{|}{C}-F + BrF_3,$$
$$[Br_2F_2] \rightarrow 2BrF \rightleftarrows {}^2/_3Br_2 + {}^2/_3BrF_3.$$

The BrF formed in the above scheme is extremely unstable and readily disproportionates to Br_2 and BrF_3.[58] Ultimately 1/3 of a mole of BrF_3 is consumed in the substitution of a single bromine atom in the bromoalkane:

$$RBr + {}^1/_3BrF_3 \xrightarrow{Br_2} RF + {}^2/_3Br_2.$$

In a recently published series of studies, it has been shown that ClF and BrF_3 smoothly substitute a bromine atom by fluorine in bromine-containing alkanes and esters.[66–70] The process is carried out at room temperature by the gradual addition of pure BrF_3 to a solution of the bromo-derivative in Freon (5–30 vol.%).[69] In the case of chlorine monofluoride, the gaseous reagent is passed through the liquid bromoalkane or its solution in an inert solvent ($CHCl_3$, CCl_4, $CF_2ClCFCl_2$) at temperatures between –50° and 50 °C.[66]

Fluorination with chlorine monofluoride and bromine trifluoride produces virtually identical results both as regards the yield and the character of the reaction products, for example:

$$CH_2ClCHBrCH_2Br \xrightarrow{ClF\ or\ 1/3BrF_3} \underset{60\%}{CH_2ClCHFCH_2Br} + \underset{20\%}{CH_2ClCHBrCH_2F}.$$

Bearing in mind that the reactions of ClF with bromo-derivatives result in the formation of elemental bromine, which is capable of reacting with ClF to form BrF_3,[58] one may assume that ClF reacts only initially with the bromoalkanes and that subsequently the fluorination is effected by BrF_3:

$$RBr + ClF \rightarrow RF + BrCl,$$
$$2BrCl \rightleftarrows Br_2 + Cl_2,$$
$$Br_2 + 6ClF \rightarrow 2BrF_3 + 3Cl_2,$$
$$RBr + 1/3BrF_3 \rightarrow RF + 2/3Br_2.$$

However, special experiments have shown that chlorine monofluoride reacts with hydrogen-containing bromoalkanes as a rule much faster than with bromine.[69]

As already mentioned previously, the opposite ratio of the rates of reaction with the organic substrate and elemental bromine (see Section V) is observed in the reactions of chlorine perchlorate with perfluoroalkyl bromides. This difference is apparently associated

with the fact that the electron density of the bromine atom of the perfluoroalkyl bromide is greatly reduced under the influence of the powerful $-I$ effect of the perfluoroalkyl group and not with the character of the oxidant (ClF and $ClOClO_3$). For this reason, substitution of bromine in perfluoroalkyl bromides is slower than the oxidation of the elemental bromine (formed as a result of the reaction) to $BrOClO_3$. On the other hand, the organic bromides used in the reactions with ClF do not as a rule have such poweful electron-accepting substituents at their reaction centre.[66,69] For this reason, in the interaction of ClF with hydrogen-containing alkyl bromides, Br_2 does not enter into a competing reaction and BrF_3 is not formed as an intermediate.[69] Virtually identical results of the substitutional fluorination with chlorine monofluoride and bromine trifluoride indicate a common mechanism of fluorination by these reagents.

The interaction of alkyl bromides with chlorine monofluoride and bromine trifluoride probably proceeds with formation of linear bromonium ions in the first stage of the reaction, which is followed by the substitution of the Br—X group by the fluoride anion or an internal nucleophile:

$$R{-}Br + ClF \rightarrow R{-}\overset{+}{Br}{-}Cl, F^- \rightarrow RF + BrCl\ ,$$

$$R{-}Br + BrF_3 \rightarrow R{-}\overset{+}{Br}{-}BrF_2, F^- \rightarrow RF + Br_2F_2\ ,$$

$$Br_2F_2 \rightarrow 2BrF \rightleftarrows {}^2/_3Br_2 + {}^2/_3BrF_3\ .$$

A characteristic feature of the reactions involving the oxidative substitution of bromine by ClF and BrF_3 is that rearrangement products are formed exclusively from primary alkyl bromides in a non-polar medium:[66,68,69]

$$CH_3(CH_2)_3CH_2Br \xrightarrow{ClF \text{ or } 1/3BrF_3} CH_3(CH_2)_2CHFCH_3\ ,$$

$$CH_3\underset{CH_3}{CH}CH_2Br \xrightarrow{ClF} CH_3\underset{CH_3}{CF}CH_3 + CH_3CHFCH_2CH_3\ ,$$

$$\underset{CH_3}{CH_2ClCFCH_2Br} \xrightarrow{{}^1/_3BrF_3} \underset{90\%}{CH_2ClCF_2CH_2CH_3} + \underset{10\%}{CH_2ClCFCH_2F}\ .$$

$$\underset{CH_3}{\quad} \qquad\qquad \underset{CH_3}{\quad}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad > 90\% \qquad < 10\%$$

Br—Cl and Br—BrF_2 are probably groups which are so readily removed that any neighbouring group, including the methyl group and the hydrogen atom, is capable of participating in the stabilisation of the resulting carbonium ion:

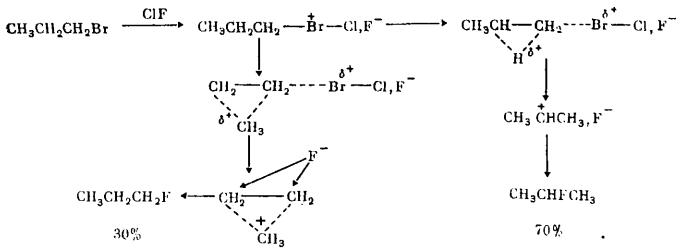
$$\underset{R}{\overset{|}{-C}}{-}CH_2Br + XF \rightarrow \underset{R}{\overset{|}{-C}}{-}CH_2{-}\overset{+}{Br}{-}X, F^- \rightarrow \underset{R^{\delta+}}{\overset{|}{-C}}{-}CH_2{-}Br^{\delta+}{-}X, F^- \rightarrow$$

$$\xrightarrow{BrX} \underset{+}{\overset{|}{-C}}{-}CH_2R, F^- \rightarrow \underset{F}{\overset{|}{-C}}{-}CH_2R\ ;$$

$$X = Cl, BrF_2 \qquad R = H, CH_3\ .$$

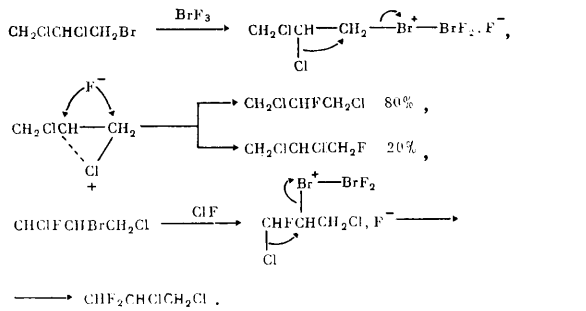
Thus it has been noted in a study of the solvolysis reactions that the degree of involvement of the neighbouring group in the stabilisation of the carbonium ion centre formed increases in the presence of neutral readily removable groups incapable of forming ion pairs.[71]

In contrast to the majority of the reactions of primary alkyl bromides, the interaction of 1-bromopropane with ClF leads to the formation of an appreciable amount of the primary fluoride, which can be explained by the involvement of the methyl group with formation of protonated cyclopropane:



The deamination of n-propylamine by nitrous acid also proceeds via the protonated cyclopropane stage.[72]

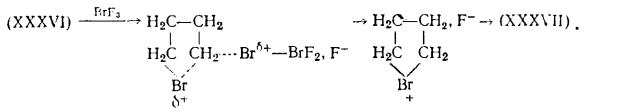
In the presence of a vicinal halogen (Br, Cl) in the substrate molecule, the halogen behaves as an internal nucleophile:



Interesting results have been obtained in a study of the interaction of 1,4-dibromobutane (XXXVI) with bromine trifluorides.[69] For the complete conversion of the initial substrate, a 50% excess of the reagent is necessary, whereupon a mixture of approximately equal amounts of the mono- and di-fluorides is formed:

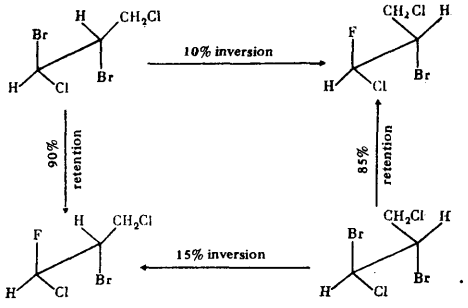
$$\underset{(XXXVI)}{Br(CH_2)_4Br} \xrightarrow{{}^1/_2BrF_3} \underset{24\%}{\underset{(XXXVII)}{Br(CH_2)_4F}} + \underset{6\%}{\underset{(XXXVIII)}{Br(CH_2)_2CHFCH_3}} + \underset{28\%}{F(CH_2)_2CHFCH_3}\ .$$

The preferential formation of 1-bromo-4-fluorobutane (XXXVII), in contrast to the reactions with primary monobromo-derivatives, indicates the involvement of bromine in the stabilisation of the carbonium ion formed



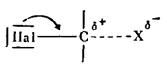
The fluorine atom is incapable of such stabilisation, as a result of which the substitution of bromine in 1-bromo-4-fluorobutane (XXXVI) takes place exclusively with a hydride shift. The presence of 1-bromo-3-fluorobutane (XXXVIII) in the reaction products confirms yet again that Br—BrF_2 is an excellent leaving group; the degree of involvement of a neighbouring group in the oxidative substitution by halogen fluorides is more likely to be controlled by a kinetic factor than by a thermodynamic factor, in contrast to the solvolysis of primary halogen-containing tosylates.[73]

The substitution of bromine by fluorine in *erythro*- and *threo*-1,2-dibromo-1,3-dichloropropanes by chlorine monofluoride takes place regiospecifically with respect to the terminal bromine atom and preferentially (85—90%) with retention of the configuration as a result of the involvement of the vicinal bromine atom:[66]



The fluorination of *erythro*- and *threo*-1-bromo-1,2-dichloro-2-fluoroethanes by chlorine monofluoride or bromine trifluoride proceeds non-stereospecifically.[66,69]

The influence of geminal and vicinal halogen atoms on the rate of the oxidative substitution of bromine by chlorine monofluoride in a non-polar medium has been investigated recently[68] by the method of competing reactions. It has been shown that the vicinal halogens greatly retard the rate of fluorination ($CH_3CHBrCH_3 \gg CH_3CH.BrCH_2Cl \gg CH_2ClCHBrCH_2Cl$). The geminal halogen atoms (Br, Cl) have only a weak influence on the rate of substitution. Thus the halogenoethanes CH_3CH_2Br and $CH_3CHClBr$ react with the monofluoride at approximately the same rates, while the accumulation of the halogens at the substituted bromine atom only slightly reduces the rate of the oxidative substitution ($CH_2BrCH_2Br : CH_2BrCHClBr : CH_2BrCCl_2Br = 10:3:1$). It is of interest to compare the results with data for the influence of the geminal and vicinal halogen atoms on the rates of solvolytic reactions proceeding via carbonium ion transition states. According to the results of Winstein and Grunwald,[74] the vicinal chlorine atom decreases the rate of solvolysis by a factor of 1000 compared with the hydrogen atom. On the other hand, geminal halogens increase the rate of reaction by stabilising the transition state:



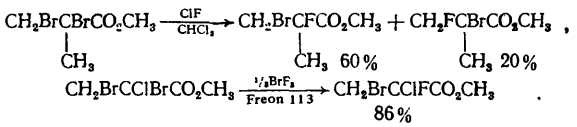
In particular, the ratios of the rate constants for the hydrolysis of benzyl bromide, 1-bromo-1-chloromethylbenzene, and 1-bromo-1,1-dichloromethylbenzene in 50% aqueous acetone are 1:6:70.[75] The geminal chlorine atom increases the rate of reaction more than does the bromine atom as a result of the powerful "back donation" effect ($C_6H_5CBr_3$‡ : $C_6H_5CClBr_2 : C_6H_5CCl_2Br = 1.0:2.4:5.6$). Analogous results have been obtained also for the hydrolysis of 2,2-dihalogenopropanes[76] ($CH_3CHBrCH_3 : CH_3CBr_2$‡$CH_3 : CH_3CClBrCH_3 = 1:6:47$). Thus vicinal halogen atoms significantly reduce the rate of both solvolysis and oxidative substitution. By increasing the rate of solvolysis, geminal halogens lower the rate of oxidative substitution. The observed difference is probably associated with the fact that the geminal halogens exert a dual influence on the rate of reaction in substitutional fluorination reactions. As a consequence of the significant inductive effect, they diminish the electron density on the substituted bromine atoms, as a result of which the rate of reaction should decrease as the geminal halogen atoms accumulate. However, the significant decrease in the rate of reaction compared with the influence of the vicinal halogens shows that the geminal halogens stabilise the transition state by diminishing the positive charge on the α-carbon atom:

‡ The rate of hydrolysis calculated per bromine atom.

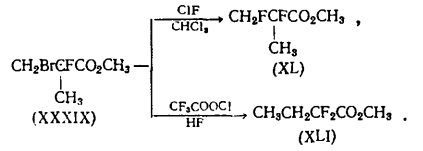


Nevertheless, the deactivating inductive effect proves stronger than the activating mesomeric effect.

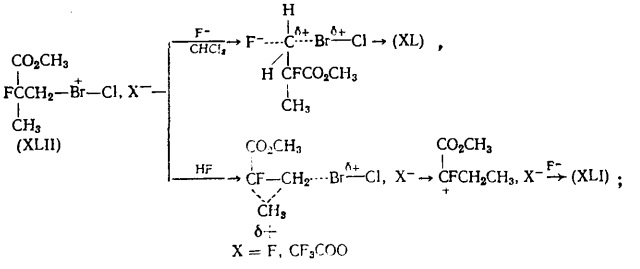
Compounds containing a functional group—esters of halogenated carboxylic acids—can be used as substrates in reactions involving substitutional fluorination by chlorine monofluoride or bromine trifluoride:[66,69]



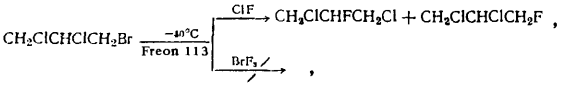
Interesting data have been obtained for the interaction of methyl 3-bromo-2-fluoro-2-methylpropanoate (XXXIX) with ClF in chloroform[66] and for the oxidative substitution of the ester (XXXIX) by the trifluoroacetyl hypochlorite–anhydrous HF system (the stoichiometric equivalent of ClF).[77] The vicinal difluoride, namely methyl 2,3-difluoro-2-methylpropanoate (XL), was obtained in a high yield in a non-polar medium, while in HF the product was methyl 2,2-difluorobutyrate (XLI), formed as a result of the 1,2-migration of the methyl group:



The result obtained can be explained by the fact that the Br–Cl group in the ion pair (XLII) formed is substituted in a non-polar medium by the fluoride ion, while hydrogen fluoride, which is a highly polar weakly nucleophilic solvent, promotes the splitting off of Br–Cl with the simultaneous migration of the methyl group:



Chlorine monofluoride is a more vigorous reagent than BrF_3. For example, whereas ClF readily substitutes the bromine atom in 1-bromo-2,3-dichloropropane at –40 °C, BrF_3 does not react under the conditions indicated:[69]



The chlorine atoms present in the substrate molecule are not as a rule involved in the reactions of ClF and BrF_3 with organic bromo-derivatives. Nevertheless, depending on the electronic properties of the substitutents in the α- and β-positions with respect to the chlorine atom to be substituted, the substitution of the latter by fluorine can

take place in a non-polar medium or in anhydrous HF.[67] In order to predict the influence of substituents on the ease of substitution of chlorine atoms in alkyl chlorides, one can undoubtedly use the result obtained in a study of the relative rates of reaction of ClF with alkyl bromides.[68] Chlorine atoms are most readily substituted when electron-donating substituents are present at the reaction centre. For this reason, the interaction of t-butyl chloride and 1,2-dichloropropane in an inert solvent (Freon 113, CCl_4) at temperatures between -30° and -50°C with an equimolar amount of ClF affords the corresponding fluorides. In the case of 1,2,3-trichloropropane and chloroform, the completion of the reaction requires an excess of the reagent:

$$(CH_3)_3CCl \xrightarrow[CCl_4,\ -60\text{—}-30^\circ C]{ClF} (CH_3)_3CF\ ,$$
$$CH_3CHClCH_2Cl \xrightarrow[-30^\circ C]{ClF} CH_3CHFCH_2Cl\ ,$$
$$CHCl_3 \xrightarrow[-50\text{—}-40^\circ C]{ClF} CHCl_2F\ .$$

Low temperatures promote the reactions by increasing the solubility and hence the concentration of chlorine monofluoride in the substrate.

The synthetic possibilities of the substitutional fluorination of organochlorine compounds increase significantly when anhydrous HF is used as the solvent.[67] Hydrogen fluoride does not then play solely the role of a highly polar solvent but also increases the reactivity of ClF as a result of the formation of the complex $Cl^{\delta+}-F-H-F^{\delta-}$.[78] The esters of chlorine-containing carboxylic acids, forming homogeneous mixtures with HF, are convenient substrates in this case:

$$CH_3CClFCHClCO_2C_2H_5 \xrightarrow[HF]{ClF} \underset{90\%}{CH_3CF_2CHClCO_2C_2H_5}\ .$$

The reactions of chloroalkanes are performed by passing ClF through a cooled stirred emulsion of the corresponding chloroalkane in anhydrous HF. Under these conditions, the oxidative substitution of the primary chlorine atom in 1,3-dichloro-2-fluoropropane is accompanied by the 1,2-hydride shift and the formation of a geminal difluoride:

$$CH_2ClCHFCH_2Cl \xrightarrow[HF]{ClF} CH_2ClCF_2CH_3\ .$$

An even greater increase in the fluorinating capacity of chlorine monofluoride is observed as a result of the use of catalytic amounts (1—5%) of antimony halides in a non-polar medium.[67] ClF then becomes so reactive that at -40 °C it substitutes the chlorine atoms in Freon 113:

$$CF_2ClCFCl_2 + ClF \xrightarrow[-10^\circ C]{SbF_5} CF_2ClCF_2Cl\ .$$

Antimony pentafluoride does not react under these conditions with Freon 113. Probably in the presence of antimony halides the fluorinating agent is the intermediate fluorodichloronium hexafluoroantimonate $Cl_2F^+SbF_6^-$—a compound analogous to $Cl_2F^+AsF_6^-$ and $Cl_2F^+BF_4^-$ described in the literature.[79]

The fluorinating capacity of BrF_3 also increases sharply in the presence of antimony halides. Tin halides can be used as effective catalysts of the fluorination of alkyl halides by bromine trifluorides.[80] Evidently, other Lewis acids, capable of producing salt-like compounds containing the BrF_2^+ cation on reaction with BrF_3, are also suitable for this purpose. The fact that the oxidising capacity of such compounds is much higher than that of the initial halogen fluorides has been demonstrated for the reactions of $BrF_2^+SbF_6^-$, $ClF_2^+BF_4^-$, $BrF_4^+SbF_6^-$, $IF_4^+SbF_6^-$, and $BrF_4^+Sb_2F_{11}^-$ with aromatic perfluoro-compounds.[81,82] The reactions proceed via a mechanism involving the one-electron oxidation of the aromatic perfluoro-substituted nucleus.[82] There is every reason to believe that such compounds should be the most powerful reagents for the substitutional fluorination of relatively unreactive alkyl halides.

Alkyl iodides react very vigorously with ClF and BrF_3 but they are not suitable substrates for fluorination by these reagents—the reactions result in complex mixtures of products, among which alkyl fluoride as well as alkyl chlorides or alkyl bromides respectively have been found.

When the *N*-bromosuccinimide—anhydrous HF system (the stoichiometric equivalent of BrF) is used as the reagent,[65] it is possible to achieve successfully the oxidative substitution of the iodine atom by fluorine in primary alkyl halides, for example, in 2,3-dichloro-1-iodopropane:

$$CH_2ClCHClCH_2I \xrightarrow[HF]{>N-Br} \underset{56\%}{CH_2ClCHFCH_2Cl} + \underset{14\%}{CH_2ClCHClCH_2F}\ .$$

The oxidative substitution of bromine atoms in tertiary and secondary alkyl bromides takes place on treatment with stoichiometrically equivalent amounts of ClF (the *N*-chloramine—HF system):[77]

$$CH_2BrCBrCH_2Cl \xrightarrow[HF]{>N-Cl} \underset{CH_3}{\overset{|}{CH_2BrCFCH_2Cl}}\ .$$

In the reactions presented, *N*-chloramine (*N*-bromamine) acts as the oxidant and HF acts as a highly polar ionising solvent and a source of fluoride anions.

VII. THE MECHANISM OF THE OXIDATIVE SUBSTITUTION

Critical examination of the original communications devoted to the reactions of alkyl halides with oxidants makes it possible to propose, in our view, the following general reaction mechanism:

$$R—Hal + X^{\delta+}—Y^{\delta-} \rightarrow \underset{(XLII)}{R—\overset{+}{Hal}—X,\ Y^-}\ ,$$
$$R—\overset{+}{Hal}—X,\ Y^- \rightarrow \text{products}.$$

The first rate-determining reaction state consists in the electrophilic attack by the reagent on the unshared electron pairs of the halogen atom with formation of the ion pair (XLII). The subsequent reaction of the ion pair can take place via several competing pathways: the first involves the substitution of the Hal—X group by the internal or external nucleophile, the second involves the addition of the anion Y^- with formation of compounds of the tervalent halogen $R-Hal\begin{matrix}X\\ \diagdown\\ \diagup\\ Y\end{matrix}$, the third involves elimination with formation of an olefin, and in the fourth Hal—X is split off with formation of a carbonium ion. The preferential occurrence of one of these reactions depends both on the halogen substituted itself and on the oxidant, the structure of the hydrocarbon group, and the reaction conditions.

The possibility of the formation of a linear halogenonium ion ($R-\overset{+}{Hal}-X$) as an intermediate species follows from the fact that halogenonium ions of analogous structure are well known.[83—85] Thus, as early as the middle of the 1950's, diarylhalogenonium salts having the general formula $Ar-\overset{+}{Hal}-ArX^-$ (Hal = I, Br, or Cl X = BF_4

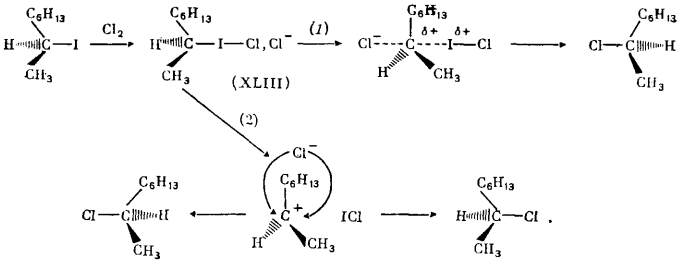
etc.) were obtained.[83] Olah and Demember[85] detected spectroscopically the formation of dialkylhalogenonium ions following the addition of a solution of antimony pentafluoride in SO_2 to an excess of the corresponding alkyl halide:

$$2R{-}Hal \xrightarrow[-60°C]{SbF_5,SO_2} R{-}\overset{+}{Hal}{-}R,\ SbF_5Hal^- ;$$
$$Hal = I,\ Br,\ Cl,\quad R = CH_3,\ C_2H_5,\ iso\text{-}C_3H_7.$$

Alkylmethylhalogenonium ions are formed when an alkyl halide is treated with the complex of antimony pentafluoride and methyl fluoride:

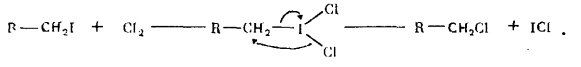
$$R{-}Hal + (CH_3F + SbF_5) \rightarrow R{-}\overset{+}{Hal}{-}CH_3\,SbF_6^- .$$

The general mechanism of the reactions of alkyl halides with oxidants discussed above makes it possible to explain satisfactorily also the majority of experimental data. Thus the formation of products with the preferential inversion of configuration on interaction of the optically active 2-iodo-octane with Cl_2, ICl, and Br_2 in methylene chloride probably takes place as follows:

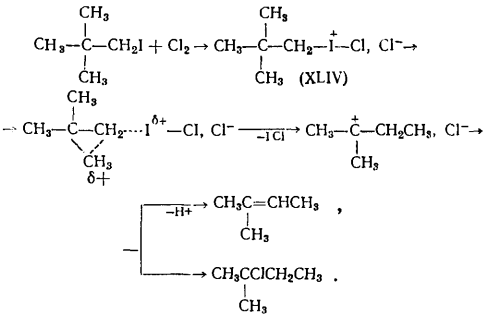


When 2-iodo-octane interacts with molecular chlorine, the ion pair (XLIII) is formed and is converted into the reaction product via two competing pathways. The main pathway (1)—the substitution of I—Cl by the chloride anion—is a usual S_N2 process which takes place with inversion of configuration. However, the I—Cl elimination reaction with formation of a carbonium ion takes place simultaneously. This is pathway (2), which in fact affords a racemic product. The increase in the yield of the products having inverted configuration following an increase in the nucleophilicity of the medium (as a result of the addition of pyridine, methanol, or diethyl ether) can be explained by the solvation of the halogenonium ion, as a result of which attack from the front becomes increasingly difficult.

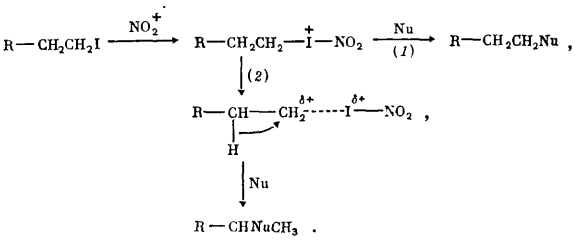
The absence of rearranged products in the interaction of chlorine and bromine with primary alkyl iodides shows that the reaction takes place exclusively via the S_N2 pathway. On the other hand, bearing in mind the fact that the interaction of alkyl iodides with Cl_2 at a low temperature leads to the formation of alkyliodine(III) dichlorides, the following alternative mechanism can be put forward:



The non-rearranged products are formed as a result of intramolecular substitution. However, the reaction of neopentyl iodide with Cl_2, which results in the formation of only a tertiary chloride and of the products of the further reaction of trimethylethylene, shows that the intramolecular substitution in alkyliodine(III) dichloride is unlikely. The interaction of neopentyl iodide with Cl_2 is consistent with the following mechanism:



For the halogenonium ion (XLIV) formed, the presence of the bulky t-butyl group in the α-position relative to the reaction centre precludes the nucleophilic attack from the rear and this is why the methyl group behaves as the internal nucleophile, i.e. the splitting off of I—Cl and the migration of the methyl group take place simultaneously. The tertiary carbonium ion formed actually affords the reaction products. An analogous picture has been observed also in the solvolysis of neopentyl derivatives[86] and it has been shown with the aid of kinetic isotope effects that the methyl group migrates in the rate-determining stage and that the successive conversion of the primary carbonium ion into the more stable tertiary carbonium ion does not occur. The reactions of primary alkyl iodides with nitrous acid and other nitrogen-containing oxidants are always accompanied by hydride shifts. This can probably be explained by the occurrence of the reaction via two competing pathways:



Depending on the reaction conditions, one of the two possible pathways can operate. Thus in the reaction in the weakly polar methylene chloride, the iodonium ion is more stable than the secondary carbonium ion formed as a result of the rearrangement and the reaction therefore takes place fully via pathway (1) (see Section III). In nitric acid, which is highly ionising weakly nucleophilic solvent, pathway (2), leading to a secondary carbonium ion, begins to predominate.

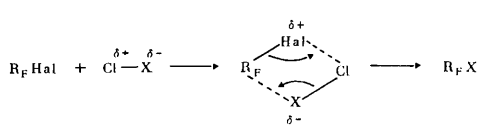
In the light of the mechanism which we propose, the general features of the oxidative substitution reactions can also be explained. Since the halogenonium ion formation stage is rate determining, it follows that the more readily is the electron pair of the halogen atom oxidised and the higher the electron density on it, the higher should be the rate of the reaction. Indeed, the reactivity of alkyl halides in reactions with any oxidant decreases in the sequence

$$-\overset{|}{\underset{|}{C}}I > -\overset{|}{\underset{|}{C}}Br > -\overset{|}{\underset{|}{C}}Cl.$$

The dependence of the reactivity on the structure of the hydrocarbon group, namely tertiary > secondary > primary, is also general. This sequence is inverted for perfluoroalkyl halides: primary > secondary > tertiary, because perfluoroalkyl substituents reduce the electron density

on the halogen atom. A characteristic feature of the reaction considered is that the structures of the products of the oxidative substitution of alkyl iodides, on the one hand, and alkyl bromides and chlorides, on the other, differ significantly. Thus the reactions of primary alkyl iodides with various oxidants (Cl_2, ICl, ICl_3, RCO_3H, HNO_3) in a non-polar medium result in the preferential formation of non-rearranged products, in contrast to the reactions of alkyl bromides with ClF and BrF_3. This is probably associated with the fact that the iodonium ion $R-\overset{+}{I}-X$, formed on oxidation of alkyl ioides, is fairly stable and that substitution takes place only on treatment with a nucleophile. It is noteworthy that the I—X group is an excellent leaving group, which is indicated by the significant involvement of the aryl substituent in the reaction of β-phenylethyl iodide with *m*-chloroperoxybenzoic acid and also by the fact that, together with the usual products, the corresponding covalent tosylates, perchlorates, triflates, etc. were isolated in the oxidative iodine substitution reactions on treatment with Cl_2, $ArCO_3H$, and NO_2BF_4 in the presence of nucleofugitive anions (TsO^-, ClO_4^-, $CF_3SO_3^-$, etc.).[87,88] However, we have observed that iodine pentafluoride in Freon 113 readily substitutes the iodine atom in 1-iodohexane with formation of 2-fluorohexane. An analogous result was obtained in the reactions of 1-bromopentane with ClF and BrF_3. Therefore the nature of the oxidant and hence the structure of the cationic intermediate probably has a decisive influence on the structure of the oxidative substitution products.

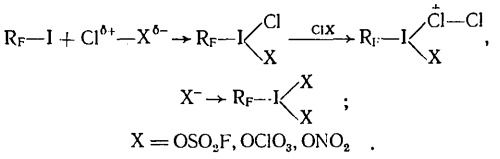
The oxidative substitution of bromine and chlorine atoms is possible only on treatment with vigorous reagents such as the hypohalite derivatives of strong acids and halogen fluorides. As a consequence of the high electronegativity of bromine and chlorine, it is inconvenient for the latter to acquire a positive charge and for this reason the halogenonium ion $R-\overset{+}{Hal}-X$, formed in the oxidation of alkyl chlorides and bromides, is extrememly unstable. The Hal—X group is readily eliminated, generating a considerable positive charge on the carbon atom, which in fact accounts for all the wide variety of rearrangements observed in the reactions with halogen fluorides. Analogous rearrangements are probably to be expected in the reactions of alkyl bromides and chlorides with the hypohalite derivatives of strong acids. However, in the substitution of chlorine and bromine atoms in perfluoroalkyl halides the accumulation of a significant positive charge on the halogen or carbon atom on oxidation is unlikely and the reaction mechanism probably therefore acquires the features of the synchronous mechanism proposed by Katsahara and Des Marteau:[50]



Hal = Br, Cl X = OSO_2F, OSO_2CF_3, $OClO_3$.

It is noteworthy that *erythro*- and *threo*-2-chloro-1,2-difluoroethyltrifluoroacetates, selected to demonstrate this mechanism, are not very suitable for this purpose, because the molecule contains the trifluoroacetate group, which can act as an internal nucleophile (see Section III). For this reason, the retention of configuration may be due to the involvement of the trifluoroacetate group and not the operation of a cyclic mechanism.

The formation of organic derivatives of tervalent iodine in reactions of perfluoroalkyl iodide with the hypohalite derivatives of strong acids can be described by the scheme

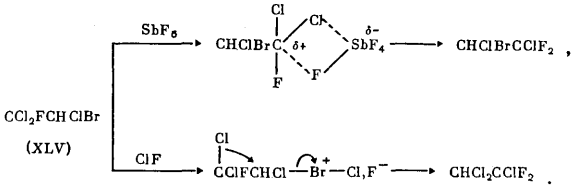


It is of interest to compare the reactions of alkyl halides with oxidants and Lewis acids such as mercury and antimony halides, silver salts, etc. The action of these reagents reduces to the conversion of the substituted halogen into a more readily eliminated group:

$$R—Hal + X^{\delta+}—Y^{\delta-} \rightarrow R—\overset{+}{Hal}—X,\ Y^- \rightarrow R—Y + HalX\ ,$$
$$R—Hal + MHal_n' \rightarrow R^{\delta+}\text{--}Hal\text{--}MHal_n'^{\delta-} \rightarrow R—Hal' + MHal_{n-1}'Hal\ .$$

In the classical solvolytic reactions, the protic solvent plays an analogous role.

However, whereas the substituted halogen atom is split off in the form of a negatively charged species in the interaction of alkyl halides with Lewis acids, on treatment with oxidants it is split off in an oxidised form. Therefore, in the interaction of polyhalogenoalkanes, the Lewis acid attacks the halogen atom whose elimination gives rise to the more stable carbonium ion, whereas the attack by the oxidant is always directed to the more readily oxidised halogen atom. Thus the interaction of 1,2-dibromo-2-chloropropane with mercury fluoride leads to the formation of 1-bromo-2,2-difluoropropane.[89] In the Swarts fluorination of 1-bromo-1,2,2,-trichloro-2-fluoroethane (XLV), only the chlorine atoms of the CCl_2F group are substituted by fluorine,[90] while on treatment of compound (XLV) with chlorine monofluoride the bromine atom is substituted with accompanying 1,2-migration of the chlorine atom:



Yet another feature of the oxidative substitution reaction consists in the fact that the halogen atom is as a rule substituted by a more electronegative atom or group. Bearing this in mind, one may say that ultimately not only the halogen atom but also the carbon atom at the reaction centre is oxidised.

The term "halogenophilic reaction" has been recently applied[91] to reactions involving the substitution of halogens on treatment with chlorine and bromine fluorosulphates. In our view, this term is inapplicable to the reactions discussed, since halogenophilic reactions are usually understood as reactions in which a halogen atom in an organic substrate is attacked by nucleophiles and the intermediate is a carbanion.[92] In oxidative substitution reactions, the halogen atom is attacked by an electrophilic species, which is followed by the nucleophilic substitution of the oxidised halogen.

Thus the reactions discussed are nucleophilic substitution reactions at a saturated carbon atom. The principal role of the oxidant consists in converting the substituted halogen into a readily eliminated group.

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During the preparation of the manuscript for the press, a study was published[93] in which the authors estimated quantitatively the oxidising capacity of a series of halogeno fluorosulphates as well as

peroxysulphuryl difluorides [$(FSO_2O)_2$] and showed that the reactivity of these compounds changes on the whole in parallel with their oxidising capacity. It was also shown that the increase in the reactivity of these compounds in a mixture with HSO_3F and HSO_3F-SbF_5 is consistent with the increasing strength of oxidants in strongly acid media.[93,94] The results obtained[93] and the proposed reaction schemes are of undoubted interest for the understanding of the mechanism of the oxidative substitution of the halogens in alkyl halides. Nevertheless, one cannot agree with the treatment of these reactions as oxidative electrophilic substitution at a carbon atom, since in electrophilic substitution at an sp^3-carbon atom the attack by the electrophile is directed to the carbon atom with which the entering electrophile subsequently forms a σ-bond. Taking this into account, the term "electrophilic substitution at a halogen atom" proposed by Katsahara and Des Marteau[50] (see Scheme 6) may be regarded as more apt. However, this definition can also be hardly regarded as acceptable for organic reactions where the carbon-containing fragment of the substrate is considered in the first place. Furthermore, in such a case the numerous nucleophilic substitution reactions occurring in electrophilic catalysis by Brønsted or Lewis acids would have to be classified as electrophilic substitutents at a heteroatom.

According to Fokin and co-workers,[93,95] the substitution of the nitroso-group in CF_3NO by chlorine fluorosulphate takes place analogously to the substitution of the halogens. One cannot rule out the possibility that the heterolytic substitution of the hydrogen atom in the C–H bond by oxidants[45,46,97] can also be interpreted as oxidative nucleophilic substitution. However, thse reactions are not numerous and are not as important as the substitution of the halogens.

In conclusion of this review, we should like to note that the reactions involving the oxidative substitution of the halogens in alkyl halides, which initially appeared to be unusual to chemists working with various oxidants and substrates, have been explained within the framework of the classical ideas of theoretical organic chemistry and have been defined as a new type of nucleophilic substitution at an sp^3-carbon atom. Many reactions of this type can be regarded as constituting yet another method for the generation of various cationoid species in polar and, what is particularly important, in non-polar media. Interesting results can apparently be obtained by using as reagents compounds such as PtF_6, $O_2^+SbF_6^-$, $XeF^+SbF_6^-$, and other "superoxidants", with an extremely high electron affinity. One may expect that further studies will make it possible to extend the synthetic possibilities of these interesting reactions and also to achieve a deeper understanding of their mechanism.

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The Synthesis and Complex Forming Capacity of Phosphorus-containing Macrocycles

E.N.Tsvetkov, A.N.Bovin, and V.Kh.Syundyukova

The review considers questions concerning the synthesis and complex-forming capacity of macrocyclic compounds containing in the ring phosphorus atoms with different degrees of coordination (from three to five) as well as macroheterocycles with phosphorus-containing side chains (lariat compounds). The introduction of the phosphoryl group into the macrocycle lowers the stability of the complexes of the macrocyclic compounds with alkali metals and reduces the selectivity compared with the analogous crown-ethers. Only the lithium cation in the case of macrocyclic phosphine oxides is an exception. Lariat macrocycles are promising: the phosphorus fragment ensures the effective additional binding of the cation imparting a high stability to the complex.
The bibliography includes 191 references.

CONTENTS

I. Introduction 776
II. Macrocyclic compounds of tricoordinate phosphorus 776
III. Macrocyclic compounds of tetracoordinate phosphorus 782
IV. Macrocyclic compounds of pentacoordinate phosphorus 789
V. Complex forming properties of phosphorus-containing macrocycles 791

I. INTRODUCTION

The discovery by Pedersen[1] in 1967 of the complex forming properties of macrocyclic polyethers (crown-ethers) in relation to alkali and alkaline earth metal cations has had a revolutionary influence on organic synthesis, which may be compared only with the influence by another major event in organic chemistry—the discovery of the method of synthesis in two-phase systems using phase transfer catalysts.[2] The discovery of crown-ethers gave rise to a powerful wave of studies not only on the use of the complex forming phenomenon in various branches of chemistry but also on the synthesis of new macrocyclic complex forming agents. Despite the fact that the principle of the macrocyclic binding of a metal was known before the discovery of crown-ethers both in the field of natural products (porphyrin and corrin complexes,[3-7] cyclic peptides, cyclic depsipeptides[8]) and among synthetic complex forming agents (phthalocyanine dyes,[9,10] certain other nitrogen-containing macrocycles[11]), only the discovery of crown-ethers has made this principle a guiding light in the search for new complex forming compounds. The "chelation" principle, which until recently predominated in the construction of new complex forming agents, became of secondary importance.

A large field of the synthesis of macrocyclic complex forming substances, which embraces increasing numbers of new elements, including phosphorus, has arisen on the basis of the new approach. The first studies on the specific synthesis of phosphorus-containing macrocyclic compounds were published in 1974 in France and in the USA. Soviet investigations on this problem began to be published since 1976. From the very beginning, two almost independent aspects arose in studies on the synthesis and properties of phosphorus containing macrocycles: (1) the preparation of macrocyclic compounds of tervalent phosphorus, mainly phosphines, and (2) the synthesis of phosphoryl macrocycles. The first aspect is related genetically to the chemistry of ligands for transition metals (phosphines and polyphosphines) and the second to the chemistry of phosphoryl extractants.

The data in the review are described in accordance with this subdivision into two aspects: the macrocyclic compounds with a tervalent phosphorus atom are described initially and this is followed by a description of the phosphoryl and thiophosphoryl macrocycles—compounds of pentacoordinate phosphorus: in conclusion, data are presented on the complex forming capacity of phosphorus-containing macrocycles.

In contrast to the reviews already published, devoted to the synthesis of phosphorus-containing macrocycles[12] and the complex forming compounds of some of them,[13] the aim of the present communication is an exhaustive description of the literature and analysis of the likely usefulness of individual aspects of the field of phosphorus-containing macrocyclic compounds.

II. MACROCYCLIC COMPOUNDS OF TRICOORDINATE PHOSPHORUS

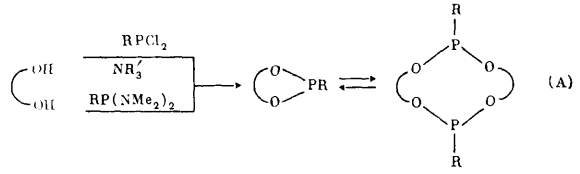
Despite the fact that the first ten-membered phosphorus-containing macrocycles of the phosphite type (acid and neutral) were obtained as early as the end of the 1940's,[14] i.e. long before the discovery of crown-ethers, specific research in this field was not begun until the 1970's. The majority of the macrocyclic tervalent phosphorus acid esters are phosphonites. These compounds have not acquired independent importance because of their instability, although they have come to be used as the starting materials for the synthesis of macrocyclic phosphonates and especially phosphonothioates, which are stable.

1. Macrocyclic Phosphonites

The principal method of synthesis of macrocyclic phosphonites [method (A)] is the dimerisation or oligomerisation of cyclic phosphonites (ring size ranging from five to eight atoms). The capacity of such compounds for oligomerisation has been frequently

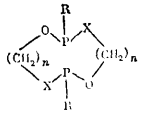
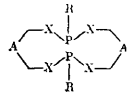
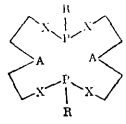
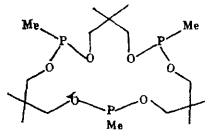
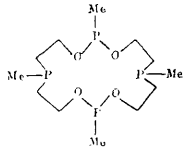
noted in the literature,[15-18] but a detailed investigation of the oligomerisation of cyclic phosphonites and their derivatives as a method of synthesis of phosphorus-containing macrocycles has been undertaken only recently.[19-29]

The cyclic phosphonites, obtained by the interaction of a diol with alkyldichlorophosphine or an alkyl phosphonodiamidite in ether, dimerise spontaneously and oligomerise:



The oligomerisation is reversible. The equilibrium shifts towards the initial compound on heating (distillation) or dilution of the solution. The macrocyclic phosphonites (I), (IIa–c), (IIIa–g), (IV), and (V), listed in Table 1, were therefore investigated mainly by NMR. The products of the addition of sulphur—the corresponding phosphonothionates—are stable compounds (they will be examined in Section III).

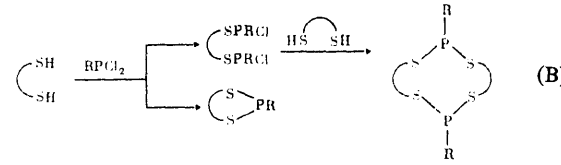
Table 1. Macrocyclic phosphonites.

Compound	Formula	Substituents	Refs.
(Ia–f)		$n = 2$, X = O, R = Me (a), Ph (b) cyclohexyl (c), t-Bu (d) X = NMe, R = Ph (e) $n = 4$, X = O, R = t-Bu (f)	[19,20] [20] [21] [25]
(IIa–e)		A = CMe_2, X = O, R = Me (a) Et (b), iso-Pr (c) A = CH_2, X = S, R = Me (d) t-Bu (e)	[22] [23] [23] [24]
(IIIa–i)		A = CH_2, X = O, R = Me (a) A = CMe_2, X = O, R = Me (b) A = S, X = O, R = Me (c) A = O, X = O, R = Me (d), Ph (e) A = NMe, X = O, R = Me (f) A = N-Bu-t, X = O, R = Ph (g) A = S, X = S, R = Me (h), t-Bu (i)	[29] [23,29] [23,29] [23,26] [29] [30] [26,27]
(IV)		—	[22]
(V)		—	[28]

The rate of dimerisation depends on the structure of the phosphonite. Dioxaphospholans dimerise fastest and are followed in this respect by dioxaphosphorinanes and dioxaphosphepans.[25] It has been shown that the oligomerisation of dioxaphosphorinanes is accelerated in the presence of the following series of substituents at the phosphorus atom:[25]

$$Ph \ll Me < Et < iso\text{-}Pr < t\text{-}Bu.$$

Dimerisation does not occur in those cases[23] where the substituent of this kind is an electronegative atom or a group of atoms with unshared electron pairs (F, Cl, OMe, OPh, NMe_2). Dithia- and diaza-phospholans and dithia- and diazaphosphorinanes do not oligomerise either.[21,23,24]† Oxazaphospholans do oligomerise;[21] the process evidently proceeds via the dissociation of the P–O bond. Despite the fact that dithiaphospholans do not dimerise, the interaction of alkyldichlorophosphine with dithiole leads not only to cyclic phosphonodithioites but also to their dimers.[23,24,27] It has been shown that the latter are formed via intermediate metastable bischlorides:



The macrocycles (IId, e) and (IIIh, i) have been obtained in this way [method (B)]. The replacement of the endocyclic oxygen atoms by sulphur stabilises the dimers so much that it is possible to isolate their *cis*- and *trans*-isomers by column chromatography [compounds (IIe) and (IIIh, i)]. Heating and/or dilution of a solution of one of the isomers of the dimer leads to the formation of the second isomer and the monomer.

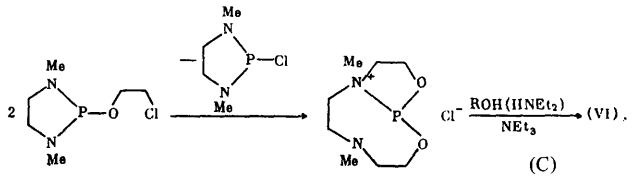
The ratio of the diastereoisomers of the 10- and 12-membered macrocycles is determined by the size of the substituent at the phosphorus atom: the macrocycle (Id), for example, is formed only as the *trans*-isomer. For the 16-membered macrocycles (IIIh, i), the ratio of the isomers becomes statistical. In the oligomerisation of 2,5,5-trimethyl-1,3,2-dioxaphosphorinane in concentrated solutions (~50%),[22] the corresponding *cis*- and *trans*-trimers (IV) were isolated together with the dimers (IIa). One should note that in all cases of oligomerisation polymeric compounds of a known structure (cyclic or linear) are also formed. Their molecular weight varies from 2000 to 15000 (established after the addition of sulphur).

2. Macrocyclic Phosphites

A sufficiently general method of synthesis of macrocyclic phosphites has not been devised. There exist only individual examples of the preparation of particular macrocycles. Thus diazaphospholans, which are incapable of oligomerising as already mentioned above, can nevertheless be used[32] for the preparation of macrocyclic phosphites in the presence of the β-chloroethoxy-group in the molecule [method (C)]. Such a diazaphospholan is converted quantitatively and spontaneously into an ammonium salt, the exchange of the chlorine atom in which by an alkoxy-group[32,33] or amino-group[34]

†The effect of the structure of cyclic compounds on their tendency to dimerise has been examined[31] from the standpoint of the concept of antibonding orbitals.

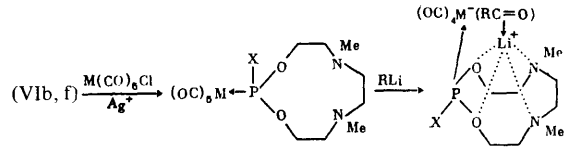
leads to the formation of 11-membered macrocycles (VI) (Table 2):



(C)

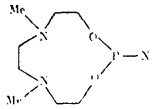
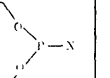
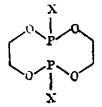
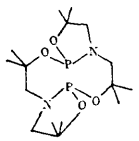
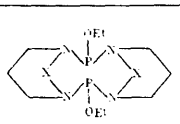
The quaternisation is accelerated in polar solvents (acetonitrile).

The complexes of the macrocycle (VI) with molybdenum or tungsten pentacarbonyls readily interact with aryl- or alkyl-lithium reagents,[34] forming lithium benzoylate or acylate complexes, which are stable by virtue of their macrocyclic nature:



The rhodium complexes obtained from the macrocyclces (VIa–e), having the composition RhCl(CO).L and $RhCl(C_2H_4).L$, are promising catalysts of the hydroformylation of olefins.[33]

Table 2. Macrocyclic phosphites.

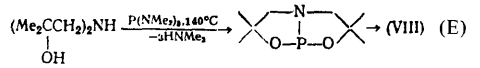
Compound	Formula	X	Refs.
(VIa–f)		OMe (a), OEt (b), OCH(Me)Et (c)	[32,33]
		OCH(Me)Pr (d), O–  (e)	[33]
		NEt_2 (f)	[34]
(VII)		OCH_2CH_2Cl	[35]
(VIII)		—	[36]
(IXa, b)		CH_2CH_2 (a), o-C_6H_4 (b)	[37]

Another method of synthesis [method (D)] of macrocyclic phosphites involves the condensation of two molecules of tri(β-chloroethyl) phosphite with liberation of dichlorethane and the formation of the dimeric phosphite (VII) (Table 2), which is entirely stable.[35]

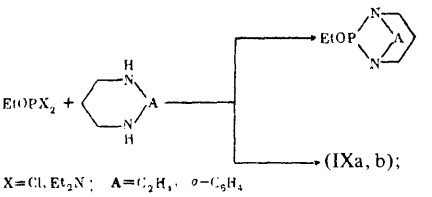
$$2\,(ClCH_2CH_2O)_3P \xrightarrow[-2ClCH_2CH_2Cl]{\Delta} \text{(VII)} \quad \text{(D)}$$

20%

In contrast to the monocyclic phosphoromonoamidites, which do not dimerise,[23] the bicyclic dialkyl phosphoramidite, obtained[36] from di(β-hydroxyalkyl)-amine and phosphorous tris(*NN*-dimethyl)triamide, is converted irreversibly and stereoselectively on heating into the dimer (VIII) [method (E)] (Table 2), whose structure has been established by X-ray diffraction:



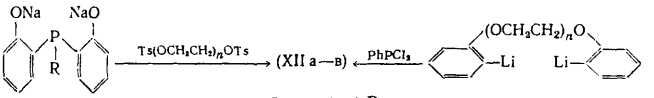
The interaction of ethyl phosphordichloridite or ethyl phosphorodi-imidite with cyclic diamines probably leads not to the expected product but to the dimer (IX) for the same reason:[37]



3. Macrocyclic Phosphines

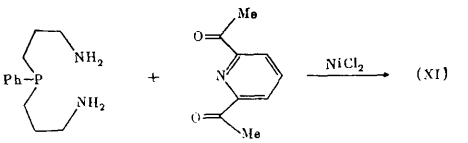
The field of macrocyclic phosphines and polyphosphines is probably the most thoroughly developed branch of the chemistry of phosphorus-containing macrocycles. More than 40 free macrocyclic ligands of the phosphine type, containing between one and four phosphorus atoms, frequently together with other heteroatoms (nitrogen, oxygen, sulphur, and arsenic), are now known. A series of macrocyclic phosphines have been obtained only in the form of transition metal complexes. Unusual catalytic properties are to be expected from complexes of this type. The stabilising capacity of macrocyclic phosphines in relation to the lowest valence states of transition metals is of interest.

The crown-ethers (Xa–c) (Table 3) containing one phosphorus atom have been obtained both by alkylating the diphenoxides of phosphorus-containing bisphenols with ditosylates of oligo(ethylene glycols) and by the interaction of dichlorophenylphosphine with organic dilithio-derivatives of polyethers:[38]



$n = 4, 5$; R=Ph, t-Bu.

A whole series of macrocycles in the form of metal complexes have been synthesised by the interaction of diketones with phosphine-containing diamines. Thus compound (XI) (Table 3) has been obtained from diacetylpyridine in the presence of $NiCl_2$:[39]



Its reduction with sodium tetrahydroborate yielded the macrocycle (XII) (Table 3). The complexes of the pentadentate macrocycle (XIII) have been synthesised analogously from diaminodiphosphines and diacetylpyridine in the presence of $Cd(ClO_4)_2$ or $AgClO_4$,[40] while the tetradentate complexes (XIVa, b) have been obtained[41,42]

Table 3. Macrocyclic phosphines.

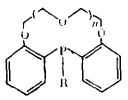
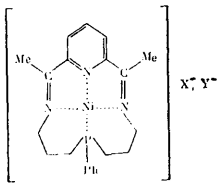
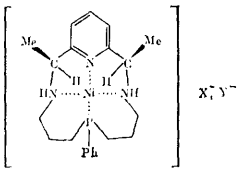
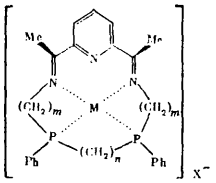
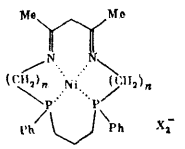
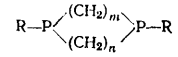
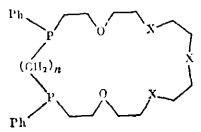
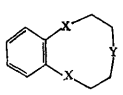
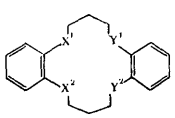
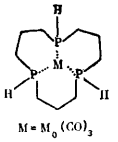
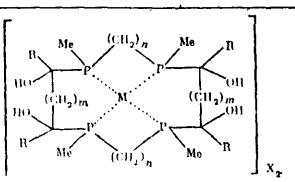
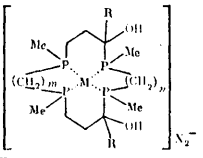
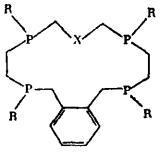
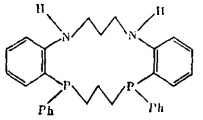
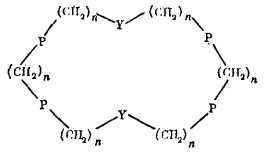
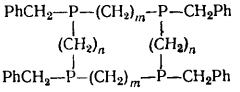
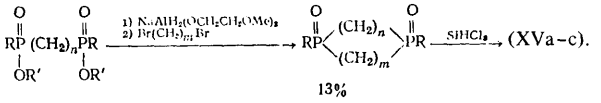
Compound	Formula	M, R, X, Y, *m*, *n*	Yields, %	Refs.
(Xa–c)		*n* = 3, R = Ph (a) *n* = 4, R = Ph (b) *n* = 3, R = t-Bu (c)	11 11 29	[38] [38] [38]
(XIa–c)		X = Br, Y = PF_6 (a) X = I, Y = PF_6 (b) X = Y = PF_6 (c)	— — —	[39] [39] [39]
(XIIa, b)		X = Y = PF_6 (a) X = I, Y = PF_6 (b)	— —	[39] [39]
(XIIIa–e)		M = Ag, *m* = 3, *n* = 2, X = ClO_4, BPh_4 (a) M = Ag, *m* = *n* = 3, X = ClO_4, BPh_4 (b) M = Cd, *m* = 3, *n* = 2, X = $(ClO_4)_2$, $(BPh_4)_2$ (c) M = Cd, *m* = *n* = 3, X = $(ClO_4)_2$, $(BPh_4)_2$ (d)	10—15 50—70 15—25 20—30	[40] [40] [40] [40]
(XIVa, b)		X = PF_6, *n* = 2 (a), *n* = 3 (b)	30, —	[41 42]
(XVa–h)		R = iso-Pr, *m* = *n* = 8 (a) *m* = *n* = 10 (b) *m* = 10, *n* = 12 (c) R = CH_2Ph, *m* = 3, *n* = 4 (d) *m* = 2, *n* = 5 (e) *m* = 4, *n* = 4 (f) *m* = 4, *n* = 5 (g) R = Ph, *m* = 4, *n* = 4 (h)	65, 81 83, 80 75, 92 78 83 80 90 89	[43] [43] [43] [79, 80] [79, 80] [79, 80] [79, 80] [79, 80]
(XVIa–c)		*n* = 3, X = NTs (a) X = NH (b) *n* = 2, X = O (c)	68 — —	[44] [44] [44]
(XVIIa–l)		X = Y = PPh (a) X = PPh, Y = S (b) X = PPh, Y = O (c) X = PPh, Y = NPh (d) X = PPh, Y = NMe (e) X = PPh, Y = CH_2 (f) X = S, Y = PPh (g) X = AsMe, Y = PPh (h) X = PPh, Y = AsPh (i) X = PH, Y = S (k) X = PH, Y = NMe (l)	34 51 32 56 42 33	[45,47] [45,47] [45,47] [45,47] [45,47] [45,47] [45,47] [48,52] [48,52] [53] [53]
(XVIIIa–h)		$X^1 = X^2 = Y^1 = Y^2$ = PPh (a) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = S (b) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = NMe (c) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = O (d) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = AsMe (e) $X^1 = Y^1$ = PPh, $X^2 = Y^2$ = S (f) $X^1 = Y^2$ = PPh, $X^2 = Y^1$ = S (g) $X^1 = Y^1 = Y^2$ = PPh, X^2 = S (h)	11, 25 45 18 38 20 — — —	[45,46,51] [45,46,51] [45,46,51] [45,46,51] [52] [52] [52] [52]

Table 3 (contd.).

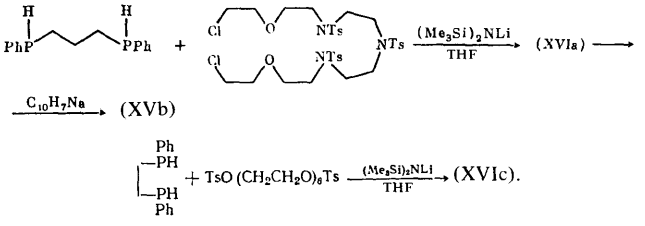
Compound	Formula	M, R, X, Y, m, n	Yields, %	Refs.
(XIX)	 $M = M_0(CO)_3$	—	85	[58]
(XXa–e)		$m = 1, n = 2$, R = H, M = Pd, X = Cl (a) R = Me, M = Ni, X = Br (b) R = Me, M = Pd, X = Cl (c) $m = 0, n = 3$, R = Me, M = Pd, X = Cl (d) R = Ph, M = Pd, X = Cl (e)	91 89 20.70 92 71	[59,60] [59,60] [59,60] [59,60] [59,60]
(XXIa–f)		X = Cl, R = H, $m = 2, n = 2$, M = Ni, Pd (a) $n = 3$, M = Ni, Pd (b) X = Cl, R = Me, $m = 2, n = 2$, M = Pd, Pt (c) $m = 2, n = 3$, M = Ni, Pd, Pt (d) X = Cl, R = Me, $m = 3, n = 2$, M = Pd (e) $m = 3, n = 3$, M = Pd (f)	91—95 91—95 91—95 91—95 91—95 91—95	[61] [61] [61] [61] [61] [61]
(XXIIa, b)		X = CH_2, R = Ph (a) X = o-C_6H_4, R = Me (b)	50 27	[62,63] [64]
(XXIII)		— —	—	[66]
(XXIVa–d)		$n = 2$, Y = O (a) Y = S (b) Y = NPr (c) $n = 3$, Y = S (d)	12 14 — 13	[67,69] [68,72] [71] [78]
(XXVa–c)		$m = 3, n = 3$ (a) $m = 3, n = 4$ (b) $m = 4, n = 4$ (c)	85 77 89	[79,80] [79,80] [79,80]

from acetylacetone in the presence of $NiCl_2$ (Table 3). The macrocycle (XIVb) has been shown to have a *meso*-structure by X-ray diffraction.

Macrocyclic bisoxides of bisphosphines have been synthesised by reducing polymethylenebisphosphinates with sodium bis(2-methoxyethoxy)aluminium hydride followed by their alkylation (without isolation) by dibromoalkanes under the conditions of high dilution (10^{-3} M).[43] Their reduction gave rise to the corresponding bisphosphines (XIVa–c), isolated in the form of *cis*- and *trans*-isomers (Table 3):

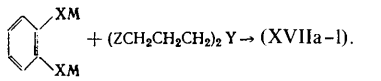


The phosphinocrown-ethers (XVIa–c) have been obtained by alkylating, under the conditions of high dilution, lithium 1,2-ethylene- and 1,3-propylenediphosphides, generated in solution, with αω-dichloro-derivatives of polyaminoethers and the ditosylates of polyether diols (Table 3):[44]



The *syn*- and *anti*-isomers of the macrocycle (XVIa) have been isolated via their complexes with $NiCl_2$. Their detosylation with sodionaphthalene takes place without isomerisation. The complex $PdCl_2.L$ has been obtained from the *anti*-isomer (XVIb), while the macrocycle (XVIc) gave rise to the complexes $NiCl_2(BF_4)_2.L$ and $Ni(NCS)_2(NCS)_2.L$.[44]

A series of 11-membered macrocyclic phosphines (XVIIa–l) (Table 3), containing between one and three phosphorus atoms in the ring together with other heteroatoms, have also been synthesised under the conditions of high dilution:[45–53]

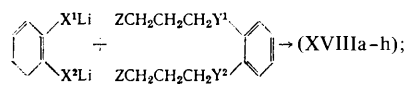


$$+ (ZCH_2CH_2CH_2)_2Y \rightarrow (XVIIa\text{–}l).$$

M = H, Li; X, Y = PH, PPh, AsPh, AsMe, NPh, NMe, S, O, CH_2; Z = Cl, Br, OSO_2Me

The study of the steric structures of compounds (XVIIa, d, e, g) established the *cis*-orientation of the phenyl substituents at the phosphorus atoms. The isomers with the *trans*-configuration were not detected even after heating under conditions promoting the inversion of the tertiary phosphines (xylene, 135 °C, 1 h). Carbonyl-containing complexes with a series of transition metals (Cr, Mo, and W)[49,50,54] and complexes with $NiCl_2$ and CuCl [50,54] have been obtained from the macrocycles (XVIIa, d, e) and the structures of some of them have been determined.[50,54] The electrochemical properties of the carbonyl complexes of the macrocycles (XVIIa, e) have been investigated.[55] Three geometrical isomers are possible for the macrocycles (XVIIh, i), but compound (XVIIh) exists only in two isomeric *meso*-forms and only one isomer has been isolated for the macrocycle (XVIIi).

The tetradentate macrocycles (XVIIIa–h) (Table 3), containing phosphorus, nitrogen, arsenic, oxygen, and sulphur atoms in the ring, have also been synthesised under the conditions of high dilution:[46,51,56]

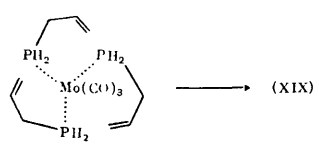


$$\rightarrow (XVIIIa\text{–}h);$$

X = PPh, S; Y = PPh, S, NMe, O, AsMe; Z = Cl, OH, OSO_2Me

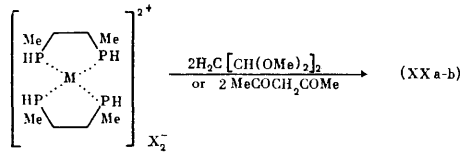
The starting compound in the synthesis of compounds (XVIIIf–h) (Table 3) was 2-(phenylphosphino)thiophenol.[56] The *cis*- and *trans*-isomers of the macrocycles (XVIIIa, f–h) have been isolated and for compounds (XVIIIf–h) the structures have also been established.[56] Four different types of complexes are formed by 11- and 14-membered ligands with cobalt halides depending on the reaction conditions and the structure of the macrocycle.[57]

A series of polyphosphine macrocycles have been obtained in the form of complexes or as free ligands by the matrix cyclisation method, i.e. by the cyclisation of phosphine ligands already bound in complexes. Thus a molybdenum tricarbonyl complex, containing three allylphosphine molecules, gives rise to a high yield of the complex (XIX) with a triphosphine macrocycle (Table 3) as a result of the intermolecular interligand free-radical addition of phosphino-groups to the double bonds:[58]



(XIX)

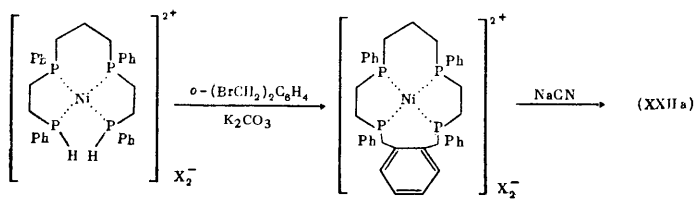
The tetradentate 14-membered cyclic adducts (XXa–c) (Table 3) have been obtained analogously by the interaction of diphosphine complexes of nickel(II) and palladium(II) with malonic dialdehyde or with acetylacetone:[59,60]



(XXa-b)

The macrocyclic complexes (XXb, c) were then obtained in the form of two isomers. The complexes (XXd, e) [59,60] and (XXIa–f) (Table 3)[61] have also been synthesised by a similar method.

Alkylation of the nickel complex of a tetraphosphine ligand with *o*-xylylene dibromide in the presence of K_2CO_3 led to the synthesis of a macrocyclic complex, from which the macrocyclic tetraphosphine (XXIIa) (Table 3) was isolated by treatment with NaCN:[62,63]



(XXIIa)

The macrocycle (XXIIb) was obtained analogously from 1,4-di-(methylphosphino)-ethane and *o*-xylylene dichloride using K_2PdCl_4 as the matrix.[64] Complexes having the compositions $PdCl_2.L$ and $NiBr_2.L$ were synthesised from this compound.[64] Alkylation of the amino-group of the nickel *meso*-complex of 1,3-di[(*o*-aminophenyl)-phenylphosphino]propane[65] made it possible to obtain the tetradentate ligand (XXIII) (Table 3).[66] The cyclic nature and *meso*-configuration of the ligand have been demonstrated by X-ray diffraction.

The 18-membered macrocyclic phosphines (XXIVa–g) (Table 3) have been synthesised by alkylating the dilithio-derivative of 1,2-di-(phenylphosphino)ethane with the corresponding dihalides containing the oxygen or sulphur atoms or the propylimino-group as the heterofragment Y:[67–75]



$$2LiPCH_2CH_2PLi + 2ClCH_2CH_2YCH_2CH_2Cl \rightarrow (XXIVa\text{–}d),$$

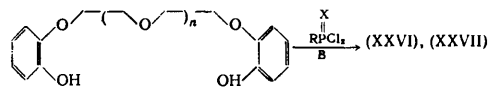
All five possible isomers have been isolated by the ion-exchange chromatography and fractional crystallisation of the metal complexes of the macrocycles. The diastereoisomers obtained show different numbers of binding sites (from 4 to 6). Their structure has been established by the X-ray diffraction analysis of the complexes of the tetraphosphines (XXIV) with the Co^{2+}, Ni^{2+}, and Fe^{2+} cations.[69–78]

A method of synthesis of the oligophosphacycloalkanes (XVd–h) and (XXVa–c) (Table 3), containing two or four phosphorus atoms, based on the reduction of the macrocyclic benzylphosphonium salts of lithium tetrahydroaluminate, has been proposed in Horner's studies.[79,80] The synthesis of the phosphonium salts themselves is examined in Section IV.

III. MACROCYCLIC COMPOUNDS OF TETRACOORDINATE PHOSPHORUS

1. Macrocyclic Phosphonates, Phosphonothioates, Phosphonimidates, and Phosphates

(a) *Macrocycles with a single phosphorus atom.* Studies on the specific synthesis and the physicochemical properties of macrocycles containing one phosphorus atom were first initiated in the USSR. The results of these investigations have been published since 1976. Macrocyclic compounds (Table 4) have been obtained by the reaction of phosphorus acid dichlorides with polyether-bisphenols:[81-90]

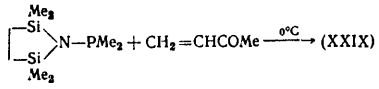


X=O, S, NSO_2Ph; $n = 1, 2$

Methyl di(β-chloroethyl)phosphonate was used as the phosphorus component in the synthesis of single phosphorus atom (Table 4), the corresponding dimers were also isolated in a number of instances (3–18%) [Table 5, compounds (XXVIIa–e)], their formation being promoted by the use of an aprotic solvent (acetonitrile).[82] The employment of the corresponding bisphenoxides instead of triethylamine increases the yield by ~10%.[83] The macrocycles (XXVIg) and (XXVIII) can be obtained only by the latter method because of the low reactivity of the phosphorus-containing fragment.[91,92] $LiClO_4$ was added as the matrix in the synthesis of compounds (XXVIc, d). The use of potassium bisphenoxide ($n = 1$) rather than sodium bisphenoxide ($n = 2$) in the reaction with methyl phosphonodichloridothioate alters the direction of the process—a mixture of the isomeric dimers (XXXVIIe) is obtained instead of the monomeric product (XXVIf) (Table 5).[83] The macrocycles (XXVIIa, b, e) have been synthesised by the high dilution method. It is of interest to note that, when lithium and potassium bisphenoxides are used in the synthesis of compound (XXVIII) instead of sodium bisphenoxide, the yield is reduced from 40 to 3–5%, which the authors believe to be associated with the matrix effect of the Na^+ cation.

The macrocycle (XXVIe) is a mixture of three polymorphic modifications, having different melting points. Their structure was investigated by IR spectroscopy.[87] The macrocycles (XXVIa, c) have been investigated by field desorption method mass spectrometry.[93]

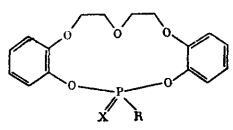
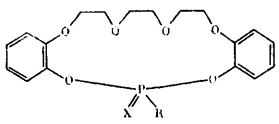
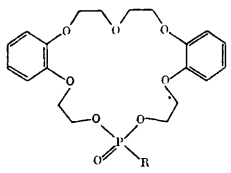
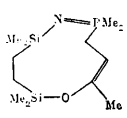
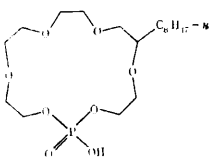
The 10-membered macrocycle (XXIX) (Table 4) has been obtained by adding methyl vinyl ketone to the cyclic phosphinic *NN*-disilylamide:[94]



The slow addition of methyl vinyl ketone to the reaction medium leads mainly to the formation of the (*Z*)-isomer, which is in its turn slowly converted into the (*E*)-isomer.

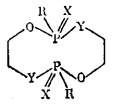
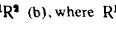
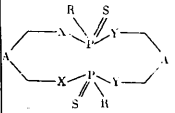
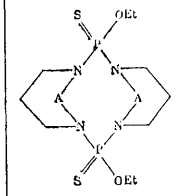
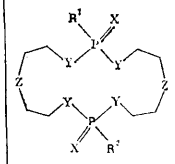
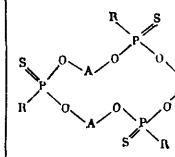
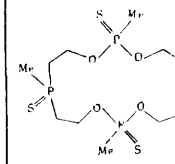
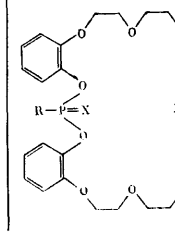
(b) *Macrocycles with two and more phosphorus atoms.* The 10-membered cyclic acid bisphosphite and the dihydrobisphosphonate (XXXIa) (Table 5) were obtained long before interest was aroused in macrocyclic complex-forming agents and an attempt was made to synthesise the acid ethylene phosphite. Later it was shown[95] that, like the cyclic phosphonites, the acid cyclic phosphites oligomerise, the process slowing down on passing from the unsubstituted acid ethylene phosphite to a substituted derivative and further to acid trimethyl phosphite. The reaction is accelerated in the presence of acids and bases. This is evidently why the interaction of phosphorus trichloride with ethylene glycol leads[14] not to the expected ethylene phosphite but to its dimer (XXXIa), which has also been obtained[35] by the condensation of two molecules of di(β-hydroxyethyl) phosphite [analogously to the method (D) for the synthesis of the macrocyclic phosphite (XII) (Table 2)]. The interaction of the diphosphite (XXXIa) with αβ-unsaturated compounds made it possible to obtain the macrocycles (XXXIb) with different side chains (Table 5), which have found applications as antipyrenes for synthetic resins:[96]

Table 4. Macrocycles with a single tetracoordinate phosphorus atom.

Compound	Formula	X, R	Yields, %	Refs.
(XXVIa–i)		X = O, R = Me (a)	17	[81.82.84]
		R = iso-Bu (b)	5	[83]
		R = Ph (c)	5	[84]
		R = OPh (d)	7	[84]
		R = N = PPh_3 (e)	22	[86.87]
		X = S, R = Me (f)	53	[84.85]
		R = Ph (g)	17	[85]
		X = NSO_2Ph, R = Ph (h)	32	[86]
		X = NSO_2Ph, R = N = PPh_3 (i)	12	[86]
(XXVIIa–g)		X = O, R = Me (a)	52	[90]
		R = Et (b)	51	[90]
		R = Ph (c)	12	[88]
		R = OPh (d)	14	[88]
		R = adamantyl (e)	—	[89]
		X = S, R = Me (f)	46	[88]
		R = Ph (g)	24	[88]
(XXVIII)		R=Me	40	[84.91]
(XXIX)		—	—	[94]
(XXX)		—	—	[168]

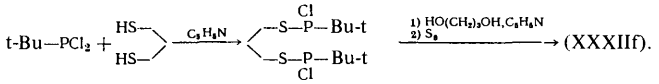
The principal method of synthesis of macrocyclic phosphonates and phosphonothioates with two and more phosphorus atoms in the ring is the oxidation of the corresponding phosphonites or the addition of sulphur to the latter. As already mentioned in the previous Section, macrocycles with tervalent phosphorus are unstable and are

Table 5. Macrocycle with two and more tetracoordinate phosphorus atoms.

Compound	Formula of macrocycle	X, Y, R, A	Refs.
(XXXIa-g)		X=O, Y=O, R=H (a) X=O, Y=O, R=$CH_2CH^1R^2$ (b), where R^1 = COOAlk, CN, $CONH_2$,  R^2=H, Alk X = S, Y = O, R = Me (c), cyclohexyl (d) R = Ph (e), t-Bu (f) X = S, Y = NMe, R = Ph (g)	[14,35] [96] [20] [19,20] [21]
(XXXIIa-h)		X = Y = O, A = CMe_2, Re = Me (a) Et (b), iso-Pr (c) X = Y = S, A = CH_2, R = Me (d), t-Bu (e) X = S, Y = O, A = CH_2, R = t-Bu (f) X = Y = O, A = CH_2, R = t-Bu (g) X = Y = O, A = CH_2, CMe_2CH_2, R = Me (h)	[22,23] [23,24] [24] [25] [23]
(XXXIIIa, b)		A = CH_2CH_2 (a), o-C_6H_4 (b)	[37]
(XXXIVa-k)		X = Z = S, Y = O, R^1 = R^2 = Me (a), Ph (b) X = S, Y = Z = O, R^1 = R^2 = Me (c), Ph (d) X = O, Y = Z = S, R^1 = R^2 = Me (e), t-Bu (f) X = Y = Z = S, R^1 = R^2 = Me (g), t-Bu (h) X = S, Y = O, Z-NMe, R^1 = R^2 = Me (i) X = S, Y = Z = O, R^1Me, R^2 = Ph (k)	[23] [23,26] [27,97] [27,97] [29] [29]
(XXXVa, b)		A=$CH_2CMe_2CH_2$, R=Me (a) A=$CH_2CH_2OCH_2CH_2$, R = Me (b)	[22] [23,29]
(XXXVI)		—	[28]
(XXXVIIa-e)		X=O, R=Me (a) X = O, R = Et (b), OEt (c) X = O, R = OPh (d) X = S, R = Me (e)	[82-84] [83] [84,93] [83,93]

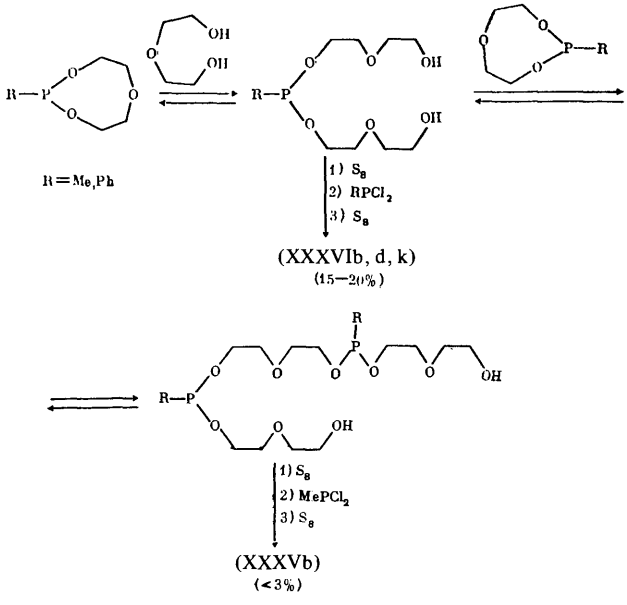
almost always isolated as phosphonates or phosphonothioates. The macrocycles (XXXIc–g), (XXXII)–(XXXIV), (XXXVa), and (XXXVI) (Table 5) have been synthesised in this way.

The stability of the bischloride, formed in the course of the synthesis of macrocyclic phosphonites [method (B)] made it possible to introduce it into the reaction with a diol and to obtain after oxidation the mixed type dimer (XXXIIf):[24]



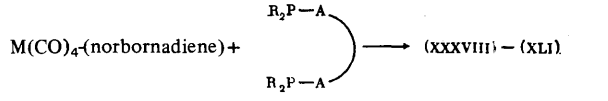
The ease of the opening of the phosphonite ring already mentioned has been used for the synthesis of the macrocyclic phosphonothioates (XXXIVc, d, k) and (XXXVb). The interaction of

diethylene glycol with an eight-membered cyclic phosphonite leads to the intermediate diol, which is capable of reacting with the next phosphonite molecule. The oxidation of phosphorus-containing polyglycols with sulphur, the subsequent interaction with alkyl- or aryl-dichlorophosphine, and the repeated addition of sulphur made it possible to obtain macrocycles containing 2–3 phosphorus atoms:[23,29]



Compounds (XXXIId, e) and (XXXIVe–h) have been studied in detail by NMR.[97] The structure of the *cis*-isomers of the macrocycles (XXXIIa) and (XXXIVh) has been confirmed by X-ray diffraction.[98,99] The complex forming properties of compounds (XXXIVe, f) in relation to uranyl nitrate and $SnCl_4$ have been investigated.[27] Among the macrocyclic dimers (XXXVIIa–e) (Table 5), compound (XXXVIIa) has been studied in greatest detail. Three isomers of this macrocycle have been isolated. The authors believe that one of the factors determining the isomerism is the steric directionality of the phosphoryl groups in relation to the polyether ring. Compound (XXVIIa) has been studied by mass spectrometry[93] and ^1H NMR using lanthanide shift reagents.[100]

The heteronuclear macrocycles (XXXVIII)–(XLI), containing a transition metal atom in the ring (Table 6), have been obtained from the polyether bisphosphites, bisphosphinates, and bisphosphinamidites by reaction with the norbornadiene complexes of molybdenum, chromium, and tungsten tetracarbonyls under high dilution conditions (in 5–70% yields):[101-103]



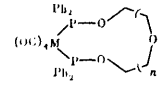
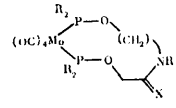
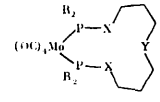
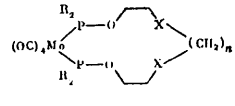
M = Mo, Cr, W; A = O, NH, NMe; R = Alk, Ar; O–Alk, OAr, NR_2

The macrocycles obtained interact effectively with alkali metal cations and form stable products of the reaction with organolithium compounds via the intermolecular coordination of lithium to the polyether ring. On hydrolysis, the latter are capable of giving rise to stable hydroxycarbenes.[104]

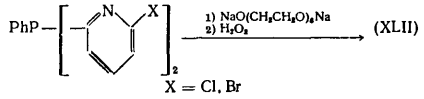
2. Macrocyclic Phosphine Oxides and Their Analogues

Among phosphoryl-containing complex forming agents, phosphine oxides are some of the most effective.[105] This is precisely why macrocyclic phosphine oxides containing, together with phosphorus,

Table 6. Phosphorus-containing macrocycles based on metal tetracarbonyls.

Compound	Formula	M, *n*, X, R	Refs.
(XXXVIIIa–c)		M=Mo, Cr, W; *n*=1 (a), 3 (b), 4 (c)	[101]
(XXXIXa, b)		*n*=2, X=H_2, R=CH_2CH_2OMe (a) *n*=3, X=O, R = H (b)	[102] [103]
(XLa–h)		X = Y = O, R = Et (a), Ph (b), R_2 = OCH_2CH_2O (c) 1,2-OC_6H_4O (d), $NMeCH_2CH_2NMe$ (e) X = Y = NMe, R = Et (f), Ph (g) X = NH, Y = NMe, R = Ph (h)	[101,103] [101,103] [101,103] [103]
(XLIa–f)		X = O, *n* = 2, R = Ph (a); R_2 = OCH_2CH_2O (b) 1,2-OC_6H_4O (c), $NMeCH_2CH_2NMe$ (d) X = NMe, *n* = 2 (e), 3 (f)	[103] [101]

other heteroatoms (O, N) have attracted special attention. Thus the phosphine oxide (XLII) (Table 7) has been synthesised by the reaction of di(halogenopyridyl)phosphine with sodium polyglycolate and subsequent oxidation of the resulting macrocyclic phosphine:[106]



Under conditions analogous to those in the synthesis of the phosphonate macrocycle (XXVIII) (Table 4), the macrocycle (XLIII) (Table 7) was obtained from sodium bisphenoxide di(chloromethyl)-methylphosphine:[107]

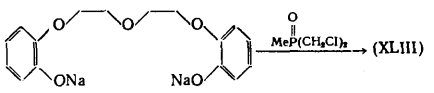
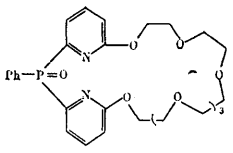
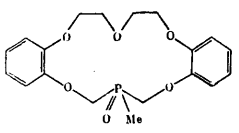
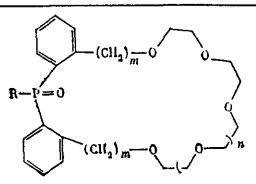
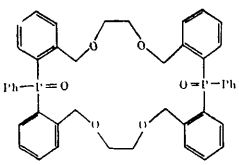
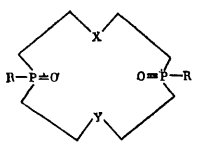
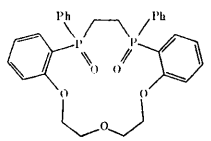
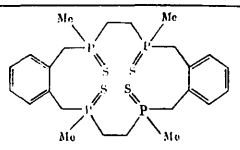
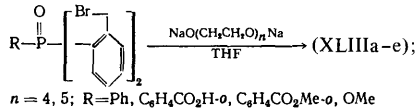


Table 7. Macrocyclic phosphine oxides and their analogues.

Compound	Formula	R, X, Y, *m*, *n*	Yield, %	Refs.
(XLII)		—	47	[106]
(XLIII)		—	15	[107]
(XLIVa-h)		*m*=0, *n*=2, R=Ph (a) *n* = 3, R = t-Bu (c), Ph (b) *m* = 1, *n* = 1, R = Ph (d) *n* = 2, R = Ph (e) *n* = 1, R = $C_6H_4CO_2H$-*o* (f) *n* = 1, R = $C_6H_4CO_2Me$-*o* (g) *n* = 1, R = OMe (h)	— — 69 67 18 — 23	[38] [38] [108] [108] [108] [108] [108]
(XLV)		—	19,22	[108]
(XLVIa-g)		R = Ph, X = Y-absent (a) R—iso-Pr, X = Y = $(CH_2)_4$ (b) X = Y = $(CH_2)_6$ (c) X = $(CH_2)_6$, Y = $(CH_2)_8$ (d) R = Ph, X = Y = CH_2OCH_2 (e) X = Y = *p*-$(CH_2O)_2C_6H_4$ (f) X = CH_2OCH_2, Y = *p*-$(CH_2O)_2C_6H_4$ (g)	— 13 13 13 — — —	[109] [43] [43] [43] [110,111] [110,111] [110,111]
(XLVII)		—	44	[112]
(XLVIII)		—	47	[64]

The phosphine oxides (XLIVa–c) (Table 7) have been synthesised by oxidising the corresponding macrocyclic phosphines (XIIa–c) (Table 3).

The interaction of di(*o*-bromomethylphenyl)-substituted phosphine oxides and phosphinic acids with sodium polyglycolates under high dilution conditions led to the formation of the macrocycles (XLIVd–h) (Table 7):[108]

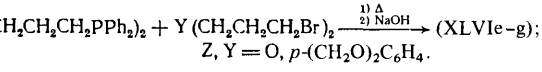


$n = 4, 5$; R=Ph, $C_6H_4CO_2H$-*o*, $C_6H_4CO_2Me$-*o*, OMe

Using ethylene glycol, the bisphosphine bisoxide (XLV) (Table 7) has been synthesised under the same conditions in the form of two isomers (apparently *syn*- and *anti*-). The above study[108] has played a major role in the elucidation of the effect of the phosphoryl group on the complex forming capacity of the macrocycles compared with other coordination centres.

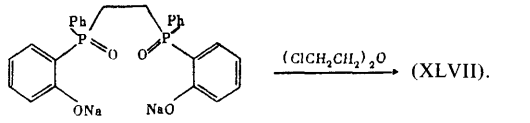
The synthesis of the bisphosphine bisoxides (XLVIb–d) (Table 7),[43] the reduction of which yielded the bisphosphines (XVa–c) (Table 3), was described in the same Section. The pairs of isomers of each macrocycle isolated after the reaction have apparently the *cis*- and *trans*-configurations.

The *trans*-isomer (XLVIa) proved to be the first phosphorus-containing macrocycle whose X-ray diffraction analysis has been carried out.[109] The macrocycles (XLVIe–g) with a more complex structure have been synthesised from an acyclic bisphosphine and the corresponding dibromide via cyclic bis-phosphonium salts (see Section IV) with the aid of the alkaline cleavage of the latter:[110,111]



Z, Y = O, *p*-$(CH_2O)_2C_6H_4$.

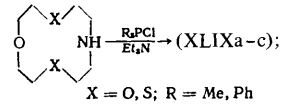
The macrocyclic bisphosphine bisoxide (XLVII) (Table 7) has been synthesised by alkylating the disodium salt of di[phenyl(*o*-hydroxyphenyl)phosphinyl]ethane with chlorex:[112]



The macrocycle (XLVIII) (Table 7) has been obtained by adding sulphur to the tetraphosphine (XXIIb) (Table 3).[64]

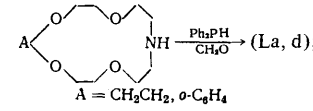
3. Macrocycles with Exocyclic Phosphorus-Containing Groups

Much attention has been devoted recently to the study of crown-ethers modified with various complex forming side groups. Macrocycles containing additional polyether groups have been called lariat (or lasso-like) ethers.[113] Similar phosphorus-containing compounds (Table 8) are obtained by modifying the usual crown-ethers. Thus the macrocyclic phosphinamidites (XLIXa–c) have been synthesised by the reaction of azacrown-ethers with dialkyl- and diaryl-chlorophosphines:[114,115]



X = O, S; R = Me, Ph

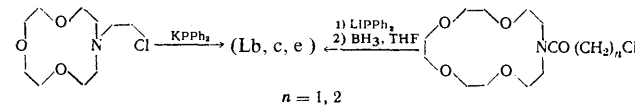
The macrocycles (La, d) (Table 8)[115,116] with phosphinomethyl side groups have been obtained in high yields by a modified Mannich reaction:



A = CH_2CH_2, *o*-C_6H_4

The macrocycle (LI) (Table 8) with four lariat phosphine groups has been obtained analogously from 1,4,8,11-tetra-azacyclotetra-decane.[117] Lariat phosphine ligands form complexes with both transition and alkali metals: complexes of the macrocycles (XLIXa, b) and (La) with Pd, Rh, Ir, Fe(0), and Cu(I) compounds and those of the ligands (XLIXc) and (Ia) with $LiPF_6$ and $NaPF_6$ respectively have been obtained.

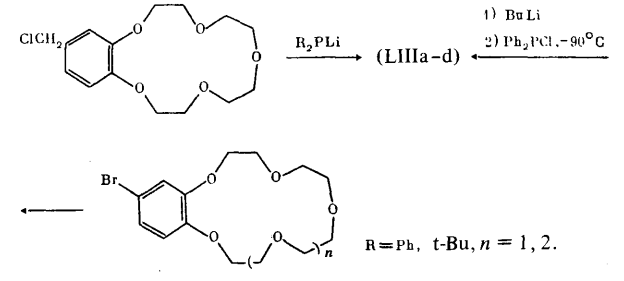
The macrocycles (Lb, c, e), in which the phosphine groups are separated from the polyether ring by 2–3 methylene units, have been synthesised by alkylating lithium (potassium) diphenylphosphite with ω-chloroalkyl derivatives of azacrown-ethers:[115,118]



$n = 1, 2$

The macrocycles (LIIa–e) (Table 8) have been synthesised similarly by the reaction of *NN'*-di(ω-chloroalkyl) derivatives of diaza-crown-ethers and diazathiacrown-ethers with potassium diphenylphosphide generated in solution from PPh_3 and potassium.[118,119] Compounds (LIIa–d) are capable of interacting with both "hard" cations of alkali and alkaline earth metals and with "soft" cations of transition metals via the phosphine. The primary coordination of the cation to the polyether ring and the oxygen atoms in the lariat groups then ensures the *cis*-configuration of the bisphosphine section in the secondary coordination to the transition metal cation. Thus a heteronuclear complex of the macrocycle (LIId) with $CaCl_2$ and $PdCl_2(PhCN)_2$ and the complex of the macrocycle (LIIb) with $Zn(ClO_4)_2$ and $Rh(nbd)_2^+ ClO_4^-$, where nbd = bicyclo[2.2.1]hepta-2,5-diene, have been obtained.[119]

The macrocycles (LIIIa–d) (Table 8)—benzocrown-ethers containing a phosphino-group in the benzene ring—have been synthesised from the corresponding chloromethyl and bromo-derivatives:[120,121]



R=Ph, t-Bu, $n = 1, 2$.

The complexes of these macrocycles with a series of rhodium, iridium, palladium, and tungsten salts have been obtained. The complexes *trans*-$PdCl_2.L_2$ and *trans*-$PdBr_2.L_2$ of the ligands (LIIIc, d) have been shown[121] to be not only reaction catalysts but also to

Table 8. Macrocycles with exocyclic phosphorus-containg groups.

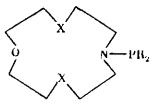
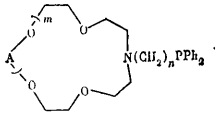
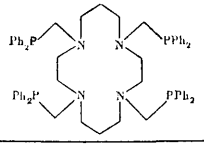
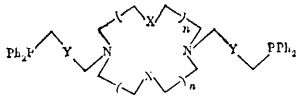
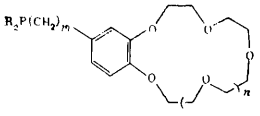
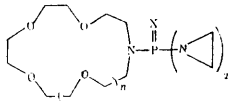
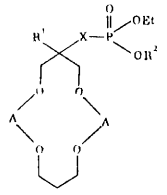
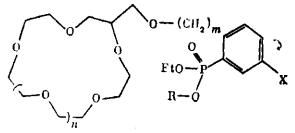
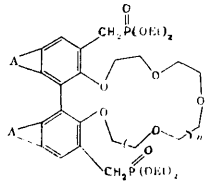
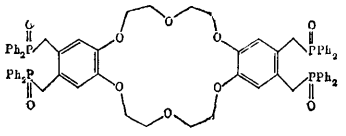
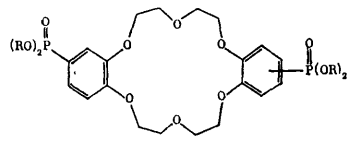
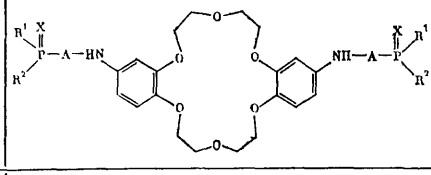
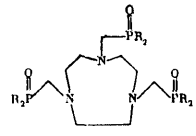
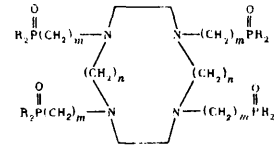
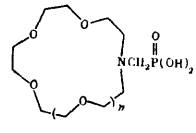
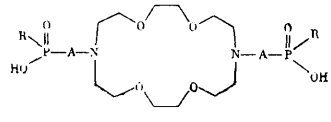
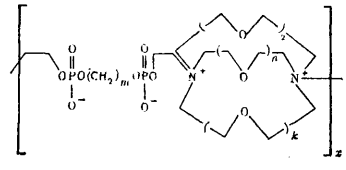
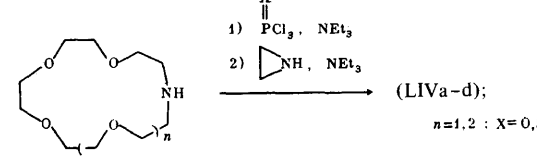
Compound	Formula	A, X, Y, R, *m*, *n*	Yield (after introduction of phosphorus)	Refs.
(XLIXa–c)		X = S, R = Me (a), Ph (b) X = O, R = Ph (c)	— 99	[114] [115]
(La–d)		*m* = 1, A = CH_2CH_2, *n* = 1 (a) *n* = 2 (b) *n* = 3 (c) *m* = 1, A = *o*-C_6H_4, *n* = 1 (d) *m* = 0, *n* = 2 (e)	98 61 34 92 41	[115,116] [115] [115] [115] [118]
(LI)		—	70	[117]
(LIIa–e)		X = S, *n* = 1, Y—absent (a) Y = CH_2OCH_2 (b) X = O, *n* = 1, Y—absent (c) Y = CH_2OCH_2 (d) X = O, *n* = 2, Y = CH_2 (e)	63 75 44 45 45	[118,119] [118,119] [118,119] [118,119] [118,119]
(LIIIa–d)		*m* = 1, *n* = 1, R = Ph (a) R = t-Bu (b) *m* = 0, R = Ph, *n* = 1 (c) *n* = 2 (d)	75 — 92 76	[120] [120] [121] [121]
(LIVa–d)		*n* = 0, X = O (a) *n* = 1, X = O (b) *n* = 0, X = S (c) *n* = 1, X = S (d)	44 63 41 18	[122] [122] [122] [122]
(LVa–e)		A = CH_2CH_2, X = CH_2CH_2O, R^1 = $C_{12}H_{25}$, R^2 = Et (a) A = *o*-C_6H_3(Bu-t), R^1 = H, X = $O(CH_2)_n$, R^2 = H, Et, *n* = 1 (b) *n* = 2 (c) *n* = 3 (d) *n* = 4 (e)	16 42 87 61 77	[123] [124] [124] [124] [124]
(LVIa–e)		*m* = 1, *n* = 1, X = t-Bu, R = H (a) *m* = 0, X = $C_{10}H_{21}$; R = H, Et, *n* = 1 (b) *n* = 2 (c) *n* = 3 (d) *n* = 4 (e)	36 71 61 61 69	[126] [125] [125] [125] [125]
(LVIIa–c)		A = $(CH_2)_4$, *n* = 1 (a) A = CH=CH—CH=CH, *n* = 2 (b) *n* = 3 (c)	84 90 97	[127] [127] [127]
(LVIII)		—	54	[128]

Table 8 (contd.).

Compound	Formula	A, X, Y, R, *m*, *n*	Yield (after introduction of phosphorus)	Refs.
(LIXa-c)		R=Et (a) R = Pr (b) R = iso-Pr (c)	67 80 71	[129] [129] [129]
(LXa-e)		A=CONH, X=O, R^1=R^2=OH (a) A—absent, X = O, R^1 = R^2 = OEt (b) R^1 = R^2 = OBu (c) R^1 = R^2 = OPh (d) X = S, R^1 = Me, R^2 = Ph (e)	— 71,24 85 53,30 72	[161] [130] [130] [130] [130]
(LXIa, b)		R=Ph (a) R = OH (b)	— 58	[131] [132, 133]
(LXIIa-c)		R=Ph, *m*=2, *n*=2 (a) R=OH, *m*=1, *n* = 2 (b) *n* = 3 (c)	63 65 85	[138] [134] [135]
(LXIIIa, b)		*n*=1 (a) *n* = 2 (b)	— 74	[136] [136]
(LXIVa-d)		A=CH_2, R=OH (a) R = H (b) A = CH_2CH_2, R = OH (c) A = CH_2CH_2O, R = OH (d)	84 74 75 69	[136,137] [137] [137] [137]
(LXVa-c)		*m*=2, 4, 6, 8, 10; *n*=*k*=2 (a); *n* = 2, *k* = 1 (b); *n* = *k* = 1 (c)	—	[139]

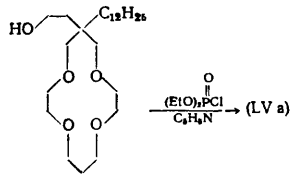
fulfill the role of phase transfer catalysts in the two-phase reduction of chloromethylnaphthalene by formic acid salts. In this case the HCO_2K complex of the ligand (LIIId) (an analogue of 18-crown-6-ether) is more active.

The macrocyclic triamides of phosphoric and phosphorithoic acids (LIVa–d) (Table 8), which exhibit antitumour activity, have been synthesised by phosphorylating monoazacrown-ethers with $POCl_3$ (or $PSCl_3$), this being followed by treatment with aziridine:[122]

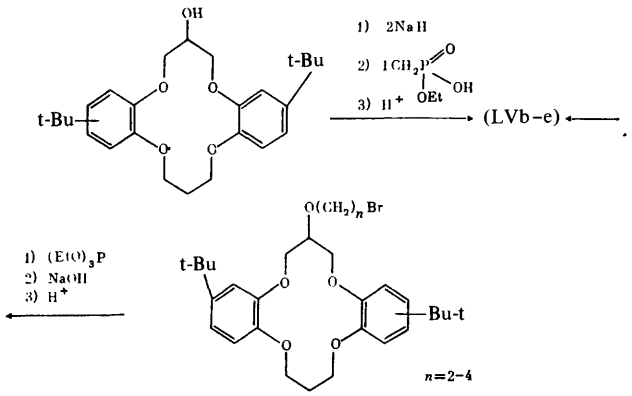


Crystalline complexes with $NaBPh_4$ have been isolated for all the complexes (LIVa–d) and have been investigated by ^{23}Na NMR.

In order to increase the lithium selectivity of 14-crown-4-ethers, its various lariat derivatives have been obtained,[123] including the macrocycle (LVa) (Table 8):

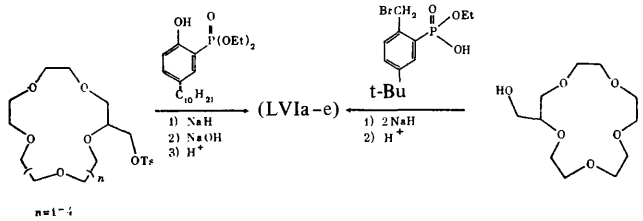


The monoethyl esters of crown-ether-substituted phosphonic acids (LVb–e) have been synthesised[124] as extractants for alkali metals from di(t-butylbenzo)-14-crown-4-ether by alkylating its hydroxy-derivative with $ICH_2PO(OEt)ONa$ [compound (LVb)] or by the reaction of the ω-bromoalkoxy-derivative of the crown-ether with triethyl phosphite [compound (LVc–e)]:



Compound (LVc) could not be obtained by alkylation [by analogy with compound (LVb)] with the aid of $BrCH_2CH_2PO(OEt)_2$ or by the addition of diethyl vinyl phosphonate.

The macrocyclic extractants (LVIa–e) (Table 8), containing the lipophilic phosphite groups, have been synthesised from the hydroxymethyl derivative of the corresponding crown-ether and the esters of *o*-bromomethyl- and *o*-hydroxyarylphophonic acids:[125,126]



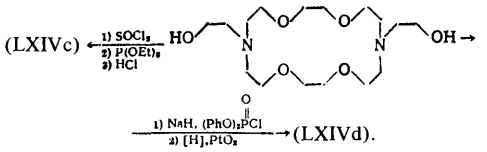
The macrocycles (LVIIa–c) (Table 8) have been synthesised by the reactions of the di(chloromethyl) derivatives of octahydrobinaphthyl-17-crown-5-ether, binaphthyl-20-crown-6-ether, and binaphthyl-23-crown-7-ether with triethyl phosphite.[127] The macrocycle (LVIII) (Table 8) has been synthesised analogously from bis-[4,5-di(bromoethyl)benzo]-18-crown-6-ether,[128] while the bisphosphonates (LIXa–c) (Table 8) have been obtained from dibromobenzo-18-crown-6-ether in the presence of nickel halides.[129]

The macrocyclic bisamides (LXa–e) (Table 8) have been obtained by phosphorylating the 4,4′-diaminodibenzo-18-crown-6-ether[130] and two polymorphic modifications of compound (LXb, c) have been isolated.

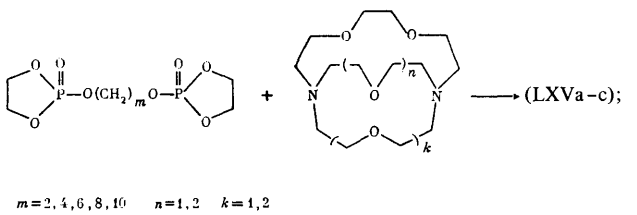
A whole series of azacrown-ethers and cyclans have been converted by reaction with paraformaldehyde (formaldehyde) and phosphorous acid or its analogues into lariat derivatives with neutral and acid phosphinylmethyl groups—the macrocycles (LXIa, b),[131–133] (LXIIb, c),[134,135] (LXa, b),[136] and (LXIVa, b).[136,137]

The octadentate ligand (LXIIa) has been synthesised by the addition of diphenylvinylphosphine oxide to 1,4,7,10-tetra-azacyclododecane.[138]

Macrocycles with acid phosphonate [compound (LXIVc)] and phosphate [compound (LXIVd)] groups have been obtained from the *NN′*-di(β-hydroxyethyl) derivative of diaza-18-crown-6-ether:[137]



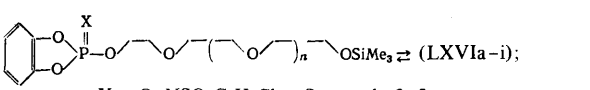
The oligomers (LXVa–c) (Table 8), capable of extracting alkali metal cations into the organic phase, have been obtained by the reaction of cyclic bisethylene phosphates with various cryptands:[139]



Their selectivity is determined by the size of the cryptand and their efficiency increases with increase in the length of the alkylene unit (*m*).

IV. MACROCYCLIC COMPOUNDS OF PENTACOORDINATE PHOSPHORUS

A series of macrocyclic pentacoordinate phosphorus compounds have been synthesised (Table 9). Here the phosphorus atom plays merely the role of a structural unit, determining in many instances the conformation of the polyether ring. Compounds of this kind have been obtained with the aid of reversible intermolecular cyclisation of *o*-phenylene phosphates or their analogues containing a poly(ethylene glycol) chain with the trimethylsilyl group in the ring:[140,141]



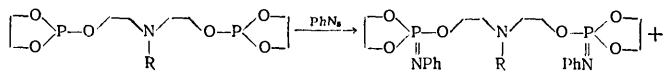
X = O, $NSO_2C_6H_4Cl$-*p*, S; *n* = 1–3, 5

The macrocycles (LXVIIa–c) (Table 9) have been obtained in an analogous way.

The cyclisation equilibrium, investigated by NMR, shifts towards the macrocyclic spirophosphorane with increase in temperature or with increase in solvent polarity. In particular the addition of pyridine stabilises the macrocyclic molecule, which the authors believe to be the result of the coordination to the phosphorus atom. However, such coordination does not cause an appreciable upfield shift of the signal in the ^{31}P NMR spectrum.[141] The tendency towards cycli-sation diminishes with increase in the length of the polyether chain and also on decrease of its conformational flexibility (after the intro-duction of the cyclohexane or benzene ring). As a

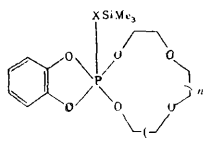
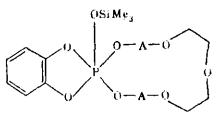
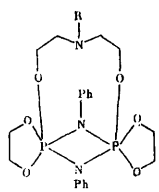
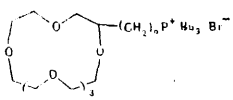
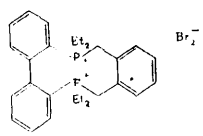
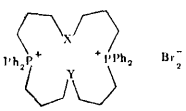
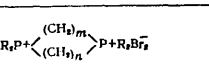
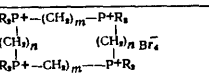
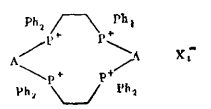
consequence of the lower affinity of silicon for nitrogen compared with oxygen, the equilibrium involving the *N*-trimethylsilyl derivatives (LXVIc, f, i) is greatly displaced towards the linear form. In the case of the thio-phosphoranes (LXVIb, e, h), the slow cyclisation is followed by the reversible dissociation of the P–OC bond in the macrocycle. The equilibrium in this process is displaced towards the quasi-phospho-nium structure. The authors believe that, according to ^{31}P NMR data, the equilibrium mixture contains also dimeric linear and cyclic phosphoranes in an amount of 1–5%.

The addition of phenyl azide to the bisdioxaphospholan phosphite entails not only the formation of a bisiminophosphoryl compound but also of its cyclisation product (LXVIIIa, b) (Table 9) as a result of the formation of the diazadiphosphetidine fragment:[142,143]



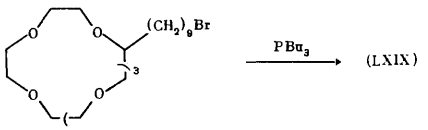
+ (LXVIIIa, b);
R = Me, t-Bu.

Table 9. Macrocycles containing a pentacoordinate phosphorus atom.

Compound	Formula	A, X, Y, R, *m*, *n*	Yield, %	Refs.
(LXVIa-i)		*n* = 1, X = O (a), S (b), $NSO_2C_6H_4Cl$-*p* (c) *n* = 3, X = O (d), S (e), $NSO_2C_6H_4Cl$-*p* (f) *n* = 5, X = O (g), S (h), $NSO_2C_6H_4Cl$-*p* (i)	— — —	[140, 141] [140, 141] [140, 141]
(LXVIIa-c)		A = CH_2CH_2 (a), *o*-C_6H_4 (b),  (c)	—	[141]
(LXVIIIa, b)		R = Me (a) R = t-Bu (b)	— 23	[142] [143]
(LXIX)		—	60	[144]
(LXX)		—	—	[145]
(LXXIa-c)		X=Y=O (a) X = Y = *p*-$O_2C_6H_4$ (b) X = O, Y = *p*-$O_2C_6H_4$ (c)	40 16 35	[110, 111] [110, 111] [110, 111]
(LXXIIa-e)		R = Ph, *m* = 3, *n* = 4 (a) *m* = 2, *n* = 5 (b) *m* = 4, *n* = 4 (c) *m* = 4, *n* = 5 (d) R = CH_2Ph, *m* = 4, *n* = 4 (e)	31 29 28 10 12	[79, 80] [79, 80] [79, 80] [79, 80] [79, 80]
(LXXIIIa-d)		R = Ph, *m* = *n* = 3 (a) *m* = 3, *n* = 4 (b) *m* = *n* = 4 (c) R = CH_2Ph, *m* = *n* = 3 (d)	9 11 20 3	[79, 80] [79, 80] [79, 80] [79, 80]
(LXXIVa-d)		X = Cl, A = CH=CH (a) A = CH_2CH_2 (b) X = Cl, PF_6, A = *p*-C_6H_4 (c) A = *p*-C_6Cl_4 (d)	80 95 85 98	[147] [147] [146] [146]

This Section presents data not only on pentacoordinate phosphorus compounds but also on phosphonium salt. Some of them have already been discussed in Sections II and III.

The macrocycle (LXIX) (Table 9), which has an exocyclic phosphonium group, has been obtained by the reaction of ω-bromononyl-18-crown-6-ether with tributylphosphine:[144]



Compound (LXIX) can effect phase transfer catalysis both in a liquid–liquid system via the phosphonium fragment and also solid–liquid phase transfer catalysis by virtue of the crown-ether fragment. However, both catalytic centres (in the reaction involving the exchange of a halogen or the cyano-group) act indpendently without synergism.[144]

The macrocyclic bisphosphonium salts (LXX) [145] and (LXXIa–c) [110,111] (Table 9) have been obtained by alkylating bisphosphine by the corresponding dibromide under the conditions of high dilution.

The bis- and tetrakis-phosphonium salts (LXXIIa–e) and (LXXIIIa–d) (Table 9) have been synthesised by the reactions of αω-alkylenebisphosphines with αω-dihalogenoalkanes and by the reactions of di(ωω′-halogenoalkyl)bisphosphonium salts with alkylenediphosphines respectively.[79,80] The use of high dilution does not increase the yield of macrocycles.

The macrycyclic phosphonium salts (LXXIVa, c, d) (Table 9) have been synthesised in an unusually high yield (80–98%) from bis(diphenylphosphino)ethane and *p*-di(chloromethyl)arenes[146] or 1,4-dichlorobut-2-ene[147] under the conditions of high dilution (10^{-2} M) on prolonged refluxing in toluene (96 h):

$$Ph_2PCH_2CH_2PPh_2 + ClCH_2{-}A{-}CH_2Cl \rightarrow (LXXIVa, c, d);$$
$$A = CH{=}CH,\ p\text{-}C_6H_4,\ p\text{-}C_6Cl_4.$$

Compound (LXXIVa) apparently the (*E*)-isomer, is formed regardless of whether the *cis*- or the *trans*-isomer of the dichlorobutene is used in the reaction. Its catalytic hydrogenation yielded the macrocycle (LXXIVb).

V. COMPLEX FORMING PROPERTIES OF PHOSPHORUS-CONTAINING MACROCYCLES

Mainly the complex-forming properties in relation to alkali and alkaline earth metal cations are considered in this Section. Data on the formation of complexes by phosphine macrocycles with transition metals are described above together with studies on their synthesis.

1. The Complex Forming Properties of Macrocycles Containing a Tervalent Phosphorus Atom

The polyether macrocycles containing a tervalent phosphorus atom, which is incapable of interacting effectively with alkali metal cations, resemble in their complex forming properties the crown-ethers having a macrocyclic ring of the same size. The stability constant and the selectivities of substances of these types are similar. For example, compounds (VIa, b) (Table 2) interact effectively with Li^+: K_s > 300 litre mol^{-1} (acetonitrile), whereas in the case of Na^+ and K^+ the stability constants fall to 8 and 5 litre mol^{-1} respectively.[148] Similarly unstable complexes with Na^+ and K^+ are formed by the macrocycles (Xa) (Table 3) and (XLIa) (Table 6). However, compound (Xc) (Table 3), differing from compound (Xa) by the substituent at the phosphorus atom (t-butyl instead of phenyl), is capable of interacting with $NaPF_6$.

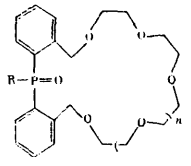
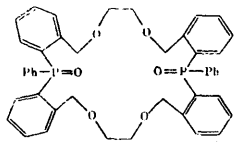
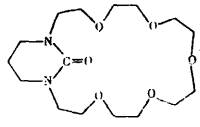
2. The Complex Forming Properties of Macrocycles Containing a Tetracoordinate Phosphorus Atom

The synthesis of phosphoryl-containing macrocycles was dictated by the endeavour to increase the efficiency of macrocyclic ligands by introducing into the ring the phosphoryl group, which possesses a high complex forming capacity. The effect of the introduction of phosphorus-containing fragments has been studied in greatest detail by Cram and co-workers.[108] Their data (Table 10) show that the introduction of the phosphoryl fragment lowers the stability of the complexes of macrocycles with Na^+, K^+, Rb^+, and Cs^+ and also the selectivity relative to the analogous crown-ethers. Only lithium is an exception in the case of the phosphine oxides (XLIVd–g) and (XLV). A decrease in the efficiency of the ligand after the introduction of the phosphorus-containing fragment into the ring can apparently be explained by the characteristics of the conformational structure of the macrocycle which prevents the cooperative interaction of all the oxygen atoms with a metal cation—the phosphoryl group is oriented away from the polyether fragment. On the other hand, the introduction of lariat carboxy-groups in the *o*-position relative to the phosphoryl group [compounds (XLIVf, g)] stabilises the complex formed. It is of interest to note that the use of the urea residue in the polyether ring [the macrocycle (LXXV), (Table 10)] leads, as in the case of the phosphoryl group, to a decrease in selectivity and in the stability constants.

The results of the study of the formation of complexes by the macrocycles (XXVI), (XXVIII), (XLVII), and (XXXVIIa) (Table 11), obtained by Yatsimirskii and Kabachnik and co-workers,[149,152] agree with the features demonstrated by Cram.[108] The compounds enumerated as well as the macrocyclic phosphine oxide (XLIII) (Table 11) [107] are inferior to crown-ethers as regards the efficiency and selectivity of their interaction with alkali metals. The "macrocyclic effect" for Li^+ is in this case insignificant, in contrast to the other cations, as can be seen from the comparison of the ligand (XLVII) with its acyclic analogue (LXXVII). The low efficiency of the phosphorus-containing crown-ethers is due to the unfavourable orientation of the phosphoryl (or thiophosphoryl) group away from the polyether ring. This conformation is energetically most favourable for the macrocycles (XXVIa),[153,154] (XXVIII),[155] and (XXVIf) (Table 4).[156]

The phosphoryl groups make the main contribution to the stability of the complex. Their decisive role in complex formation has been demonstrated by NMR for compounds (XXVIII) [152,153] and (XLIII) [157] and by IR and Raman spectroscopy for the ligands (XXVIa) [89,158] and (XXVIIe) (Table 4).[89,159] Together with the phosphoryl group, in compounds (XLIII) and (XXVIII) the oxygen atom on the opposite side of the macrocycle participates in the coordination of the cation. This conclusion is based on the chemical shift differences in the ^1H NMR spectra in the presence of lithium dinitrophenoxide for compound (XLIII) [157] and $NaClO_4$ for compound (XXVIII) [152] and also on interaction with shift reagents.

Table 10. Stability constants (10^3 K_s, M) of complexes of phosphorus-containing crown-ethers of the neutral type and their analogues with alkali metal picrates in $CDCl_3$ (24–26 °C).[108]11.

Compound	Formula	R, n	Cations				
			Li	Na	K	Rb	Cs
(XLIVd–h)		R = Ph, n = 1 (d) R = Ph, n = 2 (e) R = $C_6H_4CO_2H$-o, n = 1 (f) R = $C_6H_4CO_2Me$-o, n = 1 (g) R = OMe, n = 1 (h)	25.6 41 75 38 10	189 117 599 466 63.9	815 961 1500 3100 233	109 1040 372 461 64.6	32.3 1900 113 882 18
(XLV)		—	80	103	50	15	7,5
(LXXV)		—	71	67	240	220	150
(LXXVI)	2,3-naphtho-18-crown-6-ether	—	22.5	1220	85 990	11 300	1250

The increase by approximately an order of magnitude in lg β for Na^+ (Table 11) corresponds to the increase in the size of the cavity in the macrocycle on passing from the ligand (XLIII) to (XXVIII) for the same number of active donor centres. Compounds (XXVIIa–g) (Table 4) also interact more effectively with Na^+ than with Li^+ and K^+.[90] On the other hand, the study of the ionophoric properties of the ligand (XXVIIe) on double layer lipid membranes[89] revealed its high K^+/Na^+ selectivity. It has been suggested that a stable complex of the sandwich type analogous to the 2:1 calcium complex, in which the two phosphoryl and four (anisole) oxygen atoms are coordinated to the cation, is formed in this case.[159,160] The calculated radius of the cavity formed then corresponds to the crystallographic radius of the K^+ ion.[89] In contrast to the ligand (XXVIIe), compounds (XXVIa) and (XXVIII) form 1:1 and 1:2 calcium complexes respectively,[160] in which the cation is not shielded, as a consequence of which they do not possess an ionophoric activity.[89,161]

The stability constants of the complexes of the ligands (XLVII) [162] and (XXVIIa–g) [90] with calcium and magnesium salts have been determined by the solubility method. The thiophosphoryl macrocycles (XXVIIf, g) are weaker complex forming agents in relation to alkali and alkaline earth metals than their phosphoryl analogues (XXVIIa, c) but, like compounds (XXVIf, g), they form stable complexes with Ag^+ [85] and are effective agents for the transfer of silver picrate through a liquid dichloroethane membrane.[163]

The macrocycles (XXVIa, f),[158] (XXXVIIa),[164] and (XLVII) [165] are capable of interacting effectively with transition metal (Fe^{3+}, Cu^{2+}, Ni^{2+}, and Co^{2+}) salts and also of transporting them through a liquid membrane, which is done, for example, by the macrocycle (XXVIa) (transport of $FeCl^3$ through dichloroethane).[166]

The macrocycle (XXX) (Table 4) is an ionophore of the acid type which at pH 1.5 effectively transfers K^+ and (in the opposite direction) H^+.[167]

3. The Complex Forming Properties of Macrocycles Containing Lariat Phosphoryl Groups.

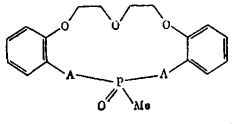
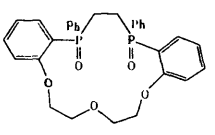
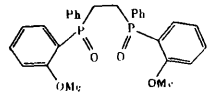
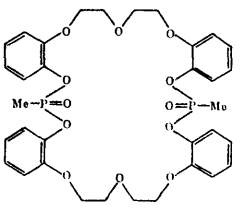
The most promising of the phosphorus-containing macrocycles at the present time are apparently crown-ethers or their analogues with phosphoryl groups in the side chain (lariat compounds). The phosphorus-containing fragment does not significantly distort the conformation of the macrocycle in this instance and hence does not disturb the effect of the cooperative interaction of the donor ring atoms with the cation. At the same time, the phosphoryl group is capable of ensuring additional binding of the cation, imparting a high stability to the complex. Thus the introduction of two phosphonate groups into the dinaphthyl residue of the crown-ether significantly increases the binding constants, as can be seen from the comparison of compounds (LVIIb, c) with compound (LXXIX) (Table 12). The values $\Delta G = -12.4$ kcal mol^{-1} for the binding of the ligand (LVIIb) to Na^+ and $\Delta G = -12.2$ kcal mol^{-1} for the formation of the complex between compound (LVIIc) and Rb^+ correspond to this kind of jump in K_s.[127] It must be emphasised that the macrocycle (LVIIb) forms the most stable complex with K^+ among the crown-ethers containing the 1,1′-binaphthyl residue.[168] X-Ray diffraction analysis has shown[169] that, in the potassium complex of the macrocycle (LVIIb) having the composition L.KSCN.$CHCl_3$, the cation is located at the centre of the polyether ring and the two oxygen atoms of the P=O groups are coordinated to it, being located on the axis

perpendicular to the plane of the polyether ring and passing through its centre. The $O_{eth}...K^+$ and $O_{P=O}...K^+$ distances are respectively 2.76 and 2.70 Å, while in most crown-ether complexes the distance exceeds somewhat 2.8 Å.[169]

In contrast to compounds (LVIIb, c), the macrocycle (LVIIa), which should be an ideal complex forming agent for Na^+ according to theoretical calculations, interacts only weakly with alkali metal cations (Table 12), although it does exhibit a very pronounced selectivity. The introduction of four diphenylphosphinylmethyl groups in the *meta*-position relative to the polyether ring in dibenzo-18-crown-6-ether [compound (LVIII, Table 13)] lowers the selectivity in relation to K^+ (cf. Table 11). However, the four additional centres, which differ from the ether oxygen atoms in the macrocycle, make it possible to obtain dimetallic complexes, such as, for example, $(CoCl_2)_2.KCl.L$,[170] in which the potassium cation is in the plane of the macrocycle and the phosphoryl groups are coordinated to the cobalt atoms.

For the lariat compound (LXIa), constructed from triazacyclononane and carrying phosphine oxide side chains (Table 13), highly stable complexes have been obtained with magnesium and calcium iodides, namely $(MgI_2)_3L_2.3H_2O$ and $CaLI_2.3H_2O$,[171] which do not decompose on heating at 100°C. Analysis of the ^1H NMR spectra of the complexes led to the conclusion that all the nitrogen atoms of the ligand in the Mg^{2+} complex are involved in coordination to the metal, whereas in the Ca^{2+} complex only one nitrogen atom interacts with the cation. The different stabilities of the complexes are indicated also by the values of $\lg K$ for MgI_2 and CaI_2—2.8 and 2.4 respectively (1:1 acetonitrile–$CHCl_3$ mixture).[171] The study of complex formation with alkali metals showed that the macrocycle (LXIa) forms a highly stable complex with Li^+: $\lg\beta = 5.6$ (4:1 THF–$CHCl_3$ mixture).[131] The higher selectivity of the compound with respect to lithium compared with the simplest analogues, for example, compound (LXXX) (Table 13) is caused, according to the authors, by the flexibility of the lariat molecule, which enables it to

Table 11. The logarithms of the stability constants ($\lg\beta$) of complexes of phosphorus-containing crown-ethers with alkali metal cations.

Compound	Formula	A	Cations				Anion	Solvent	Refs.
			Li	Na	K	Cs			
(XXVI a)		O	1.2	—	—	—	Cl	MeCN	[149]
(XXVIII)		OCH_2CH_2O	2.25	2.36	—	—	ClO_4	acetone	[152]
(XXVIII)		OCH_2CH_2O	3.36	4.23	—	—	picrate	THF/DCE	[151]
(XLIII)		CH_2O	3.26	3.29	3.29	2.56	2,4-dinitrophenoxide	THF/$CHCl_3$	[107]
(XLVII)		—	2.30	2.13	2.04	2.02	acetate	EtOH/$CHCl_3$	[150]
		—	2.70	—	—	—	Cl	MeCN	[150]
		—	2.81	3.42	2.85	2.26	I	MeCN	[150]
		—	3.12	2.64	1.78	—	ClO_4	MeCN	[150]
(LXXVII)		—	1.64	1.59	1.56	1.51	acetate	EtOH/$CHCl_3$	[150]
			3.08	2.46	1.88	0.4	I	MeCN/$CHCl_3$	[150]
			3.18	2.01	0.3	—	ClO_4	MeCN/$CHCl_3$	[150]
(XXXVII a)		—	1.9	1.7	1.0	0.3	acetate	EtOH/$CHCl_3$	[149]
			3.0	—	—	—	Cl	MeCN/$CHCl_3$	[149]
			2.7	—	—	—	I	MeCN/$CHCl_3$	[149]
(LXXVIII)	Dibenzo-18-crown-6-ether	—	3.48	3.97	4.51	3.47	Cl	EtOH/$CHCl_3$	[170]
			4.06	5.60	4.66	3.3	2,4-dinitrophenoxide	THF/$CHCl_3$	[138]

assume the energetically most favourable conformation. The linearity of the relation between $\lg\beta$ and $1/r$ (where r is the ionic radius of the cation) indicates the ion–dipole character of the interaction, i.e. the electrostatic interaction of the cation with the polar groups of the ligand makes the main contribution to the free energy change.[131]

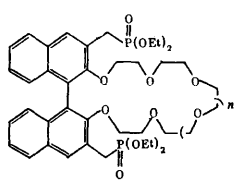
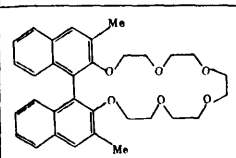
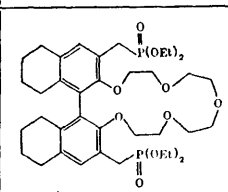
In contrast to the macrocycle (LXIa), the phosphinylethylated tetra-azacyclododecane (LXIIa) (Table 13) interacts preferentially with Na^+ and is significantly superior to dibenzo-18-crown-6-ether (Table 11) as regards efficiency and Na^+/K^+ selectivity.[138] Complexes with cobalt salts have been obtained for both compound (LXIa) [172,173] and the macrocycle (LXIIa).[173]

The acid analogue of compound (LXIa) [the macrocycle (LXIb), Table 8)] does not form stable complexes with alkali metal cations in water but it does interact effectively and selectively with doubly charged cations having a small radius.[132,133] Thus the difference between the stability constants of the complexes with Mg^{2+} and Ca^{2+} is by about 5 orders of magnitude (the $\lg K$ for the complexes ML are respectively 11.01 and 6.38). A high selectivity is observed also in the series of Group II B transition metals: the complex with Zn^{2+} (r = 0.74 Å) formed by the ligand is the most stable among all those known for zinc ($\lg K$ = 24.9 for the complex ML). The stability constant for Cd^{2+} (r = 0.97 Å) is lower by five orders of magnitude. A very stable complex is also formed with the Fe^{3+} ion (r = 0.64 Å): $\lg K$ = 29.6 for the complex ML. According to X-ray diffraction data,[174] the Fe^{3+} cation in the complex is located in the inner cavity of the ligand, formed by the side groups, and interacts with all its donor centres. The "twisted basket" conformation produced under these conditions differs in energy from the conformation in the free state by only ~5 kJ mol^{-1}.[175]

The tetraphosphinic acid (LXIIb) (Table 8), whose ring has been increased by one aminoethyl unit, has a completely different spectrum of interaction with cations:[134] whereas complexes of the ligand (LXIb) are more stable for cations with an ionic radius $\leqslant$0.7 Å, cations with a radius >0.8 Å form more stable complexes with the ligand (LXIIb). For example, the macrocycle (LXIIb) forms a more stable complex with Ca^{2+} than with Mg^{2+} (the $\lg K$ for the complexes ML are 10.3 and 7.3 respectively). The ligand (LXIIb) is a selective complex forming agent for Cd^{2+} and Pb^{2+}, but, in relation to a whole series of cations, including alkaline earth metals, it is greatly inferior to the carboxyl-containing analogue 1,4,7,10-tetrakis-(carboxymethyl)-1,4,7,10-tetra-azacyclododecane, and also to the macrocycle (LXIb), and is close to the relatively weakly selective complexone EDTA. Atom–atom potential function calculations have shown[175,176] that the low selectivity of compound (LXIIb) can be explained by the adequate conformational possibilities for the formation of six- and five-coordinated complexes with various cations. The maximum number of binding sites (eight) is not utilised owing to the mutual repulsion of the phosphenyl group. Like compound (LXIb), the macrocycle (LXIIb) forms relatively unstable complexes with the alkali metal cations, the stability decreasing in the sequence $Li^+ > Na^+ > K^+$. For the K^+ cation, $\lg K < 1$.[134]

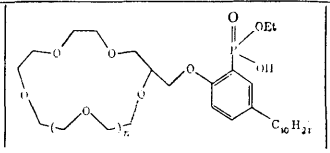
The "expansion" of the ring in the ligand (LXIIb) by two methylene units [to give compound (LXIIc), Table 8] and hence the increase in its conformational mobility lead to a sharp decrease (by 6–8 orders of magnitude) of the stability of the complexes with all cations.[135] For example, $\lg K < 2$ for alkaline earth metal cations (for the ML complexes). The carbonyl-containing analogue of compound (LXIIc)—1,5,8,12-tetrakis(carboxymethyl)-1,5,8,12-tetra-azacyclotetradecane—is only slightly inferior to it as regards efficiency, but the difference between the values of $\lg K$ for the two ligands in the case of Cu^{2+} reaches 8 orders of magnitude. The high selectivity of compound (LXIIc) with respect to the Cu^{2+} ion ($\lg K$ = 26.6 Cu^{2+} and $\lg K$ = 15.6 for Ni^{2+}) is probably favoured by the

Table 12. Stability constants (10^{-3} K_s, M) of complexes of phosphonate lariats of the neutral type with alkali metal picrates in $CDCl_3$.[127]

Compound	Formula	n	Cations				
			Li	Na	K	Rb	Cs
(LVIIb)		1	136	$1.16\cdot10^6$	$8.39\cdot10^5$	19500	2520
(LVIIc)		2	320	830	$5.8\cdot10^5$	$1.1\cdot10^6$	23200
(LXXIX)		—	228	1730	$4.28\cdot10^4$	4700	576
(LXIIa)		—	33	620	12	4.5	2.75

stable conformation, found by the method of atom–atom potential functions. The nitrogen atoms in it form a planar square and the phosphono-groups in the apical positions can additionally stabilise the complex.

Table 14. The competitive extraction of alkali metal chlorides from 0.25 M aqueous solutions into a 0.05 M ligand solution in $CHCl_3$ (in %) at pH 9.[125]

Compound	Formula	n	LiCl	NaCl	KCl	RbCl	CsCl
(LVIb)		1	5	50	21	14	5
(LVIc)		2	—	—	57	24	5
(LVId)		3	10	12	17	31	30
(LVIe)		4	11	22	23	18	20

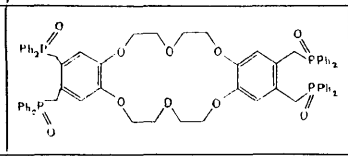
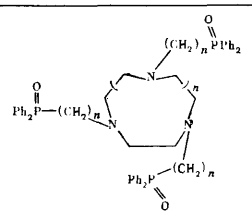
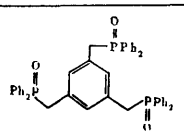
In contrast to the ligands (LXIb) and (LXIIb, c), the *N*-dihydroxyphosphinylmethylated azacrown-ethers (LXIIIa, b) and (LXIVa) (Table 8) form more stable complexes with Na^+: $K_{NaL} = 20-40$.[136] The presence of at least one phosphonate group is essential for the formation of stable complexes, since unsubstituted monoaza- and diaza-crown-ethers do not interact with Na^+. Macrocycles with five heteroatoms in the ring [compound (LXIIIa)] are the most effective, which is particularly characteristic of the carboxy-analogues of compound (LXIVa).

The macrocycle (LXIVa) and its analogues with carboxy- and phosphonite groups [compound (LXIVb), Table 8] proved to be promising solubilising agents for barium sulphate.[137] Their efficiency in relation to the [2.2.2]cryptand is 65, 65, and 19% respectively. The use of longer phosphonoalkyl and carboxyalkyl chains or other polar groups (SO_3H, OPO_3H_2, OSO_3H) lowers sharply the solubility of the Ba^{2+} complexes.

The introduction of a lariat phosphoryl-containing group [the macrocycle (LVa), Table 8] or of the amino-group into 14-crown-4-ether increases its selectivity with respect to lithium.[123] The selectivity coefficients in a polymer membrane then reach 182 (Li^+/Na^+) and 288 (Li^+/K^+). On the other hand, ester and 8-hydroxyquinoline groups impair the selective properties of the crown-ether.

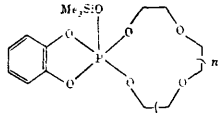
A whole series of crown-ether-substituted phosphonic acids have been investigated as extractants of alkali metal cations.[124–126] Thus, among phosphinylalkoxy-derivatives of di(t-butylbenzo)-14-crown-4-ether (LVb–e) (Table 8), a highly selective extractant for Na^+ has been found, namely the ligand (LVc).[124] A further increase in the length of the alkyl chain between the polyether ring and the charged phosphonate group leads to the loss of selectivity and to a decrease in the efficiency of the extractant [compounds (LVd, e)]. As shown on models, the length of the lariat group in compounds (LVc) is optimum from the additional stabilisation of the sodium complex. The macrocycles (LVIb–e) (Table 14),[125] containing the lipophilic

Table 13. Logarithms of the stability constants ($\lg\beta$) of complexes of phosphorus-containing lariats of the neutral type and their analogues with alkali metal cations.

Compound	Formula	n	Cations				Anion	Solvent	Refs.
			Li	Na	K	Cs			
(LVIII)		—	3.09	3.86	3.95	3.47	Cl	EtOH/$CHCl_3$	[170]
(LXIa)		1	5.6	4.5	3.2	2.2	2,4-dinitrophenoxide	THF/$CHCl_3$	[131]
(LXIIa)		2	5.91	6.29	5.04	3.6	2,4-dinitrophenoxide	THF/$CHCl_3$	[138]
(LXXX)		—	5.1	4.4	4.0	3.3	2,4-dinitrophenoxide	THF/$CHCl_3$	[131]

phosphonate group, extract cations in conformity with the size of their polyether ring. For example, the macrocycle (LVIb), constructed from 15-crown-5-ether, extracts Na^+ preferentially. Compound (LVIa) (Table 8) behaves analogously. The formation of its highly stable sodium complex has been demonstrated by ^1H NMR.[126] The principal advantage of the phosphorus-containing extractants investigated compared with their carboxy-analogues is their higher efficiency and also their ability to extract cations at low pH (down to pH 2).

Table 15. The solubilities of alkali metal chlorides (mole % relative to the ligand) in 0.1 M solutions of the macrocycles in dichloroethane (20 °C).[141]

Compound	Formula	n	LiCl	NaCl	KCl	RbCl	CsCl
(LXVIa)		1	25.2	1.9	0.1	—	—
(LXVIIa)		2	34.4	0.6	0.5	—	—
(LXVId)		3	43.9	0.6	0.5	—	—
(LXVIg)		5	52.1	3.4	3.3	3.7	1.7
(LXXXI)	18-crown-6-ether		2.7	2.7	17.3	—	—

4. The Complex Forming Properties of Macrocycles Containing a Pentacoordinate Phosphorus Atom

The formation of complexes by the macrocycles (LXVIa, d, g) and (LXVIIa) (Table 15), containing the phosphoranyl group, with alkali metal chloride has been investigated by the solubility method.[141] In contrast to compound (LXVI) (n = 0), which does not possess complex forming properties because of its small ring size, the macrocycles (LXVIa, d, g) and (LXVIIa) interact selectively and effectively with Li^+, being greatly superior in this respect to 18-crown-6-ether. With increase in ring size and in the number of ether oxygen atoms on passing from compound (LXVIa) to (LXVIg), the efficiency of the complex formation with LiCl also increases. On the other hand, the interaction with cations having larger radii (Na^+, K^+, Rb^+, Cs^+) is weaker, even for the 23-membered macrocycle. The authors explain the selectivity with respect to Li^+, especially for compounds (LXVIa, d) and (LXVIIa), by the fact that the trigonal-bipyrimidal configuration of the phosphorus atom imparts to the conformationally labile ring a geometry in which the donor oxygen atoms are not in a single plane and the size of the cavity formed by them corresponds only to the lithium cation. The disadvantage of the phosphorane macrocycles is their hydrolytic instability.

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During the preparation of the manuscript for the press, new studies on the synthesis and complex-forming properties of phosphorus-containing macrocycles were published. Thus macrocycles with phosphorus(III) have been obtained by the transamidation of the amide $PhP(NMe_2)_2$ or $P(NMe_2)_3$ with polyetherbisamines containing *o*-aminophenol or 3-amino-2-methoxybenzyl alcohol fragments as the end group. They were converted by oxidation or the addition of sulphur into the corresponding macrocycles with phosphorus(IV).[177] A tetraphosphorus(III) macrocycle has been synthsised in a high yield in the form of the nickle complex by the matrix cyclisation method from the phosphine complex $PhP[(CH_2)_3PhMe]_2.NiBr_2$ and the amide $Et_2NP(CH=CH_2)_2$ [cf. the ligand (XIX) (Table 3)] in a high yield. The nickel complex was then oxidised to the phosphorus(IV) derivative.[178] A 22-membered bisphosphonate macrocycle has been obtaind[179] in 6–8% yield from *OO'*-di(β-hydroxyethyl)-catechol and $MeP(O)Cl_2$ by the same method as compound (XXXVIIa–e) (Table 5). The stability of its complexes with alkali metals varies in the sequence Na > Li ≫ K. The complex-forming properties of the macrocycles (XXVIa, c), (XXVIIa, c), (XXVIII), and (XXXVIIa) in relation to the lithium, sodium, potassium, magnesium, and calcium cations have been investigated by a modified solubility method in the CH_2Cl_2 + 2% MeCN mixture.[180] The extraction of sodium, potassium, magnesium, calcium, strontium, barium, and other metals by chloroform solutions of the macrocycles (XXVIa, f), (XXVIIIa, e, f), and (XXXVIIe) has been studied.[181] In contrast to the phosphonate crown-ethers, which possess no extracting properties, the phosphonothionates (XXVIf), (XXVIIf), and (XXXVIIe) extract to a slight extent silver, mercury, and palladium at pH 1–5 and extract them quantitatively from concentrated acid solutions. Phosphate ionophores of the acid type—compound (XXX) (Table 4) and five of its analogues—have been obtained by the interaction of oligo(ethylene glycols) with $POCl_3$ under high dilution conditions (5×10^{-2} M) with subsequent hydrolysis of the resulting cyclic phosphoromonochloridate[182] [demonstrated in relation to compound (XXX)]:

$$HOCH_2CH_2OCH(CH_2OCH_2)_3CH_2OH \xrightarrow[2)\ H_2O,15^\circ C]{1)\ POCl_3,\ -70^\circ C} (XXX)$$
$$\quad\quad\quad

Methods of synthesis have been developed for phosphorane macrocycles. Such compounds with two and more phosphorus atoms can be obtained by the reaction of the disilyl ethers of alkane-αω-diols with $PhPF_4$ [189] or of the diols themselves with Ph_3P in the presence of di-isopropyl azodicarboxylate.[190,191]

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Dissociation of Water Molecules in Systems with Ion-exchange Membranes

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The principles of the dissociation of water molecules in membrane systems containing cation-exchange, anion-exchange, and dipolar membranes are examined. The characteristics of the attainment of the limiting state at the membrane-solution boundary and the differences in the behaviour of cation-exchange and anion-exchange membranes are discussed from the standpoint of the possibility of the dissociation of water at the interfaces. The mechanisms and the kinetics of the dissociation of water in membrane systems involving catalytically active centres† are considered.
The bibliography includes 87 references.

CONTENTS

I. Introduction 801
II. Dissociation of water molecules at the membrane-solution boundary 801
III. Dissociation of water molecules in dipolar membranes 804

I. INTRODUCTION

The problem of the dissociation of water molecules in a membrane system when an electric current flows through the latter is one of the central problems in the electrochemistry of membranes. This is associated with the complications arising from the dissociation of water in membrane systems and with the new possibilities for electrochemical technology opened up by its use. In the demineralisation of solutions by electrodialysis, the dissociation of water in the region of the membrane–solution boundary leads to the participation of the H^+ and OH^- ions in transport across cation-exchange and anion-exchange membranes. As a consequence of this, the limiting current decreases,[1] there is an additional consumption of electrical energy on demineralisation, the pH changes in the electrodialyser chambers, and chemical reactions sensitive to changes in the acidity of the medium occur, including the crystallisation of calcium carbonate and magnesium hydroxide in the concentration chambers, where the pH is in excess of 7, or reactions sensitive to the precipitation of silicic acid in the desalination chambers, in which the medium is acid.

Since the transport of the water dissociation products across the membrane begins after the attainment of the limiting state when the concentration of the H^+ and OH^- ions in the region of solution near the membrane becomes comparable to the electrolyte concentration,[2–4] attention has been concentrated on the search for signs preceding the onset of limiting state in order to have reliable ways of maintaining the membrane system in the pre-limiting state, where water does not decompose.

Recently there has been a growth of interest in the decomposition of water in membrane systems for several reasons. Firstly, this is associated with the appearance of dipolar membranes and their use in electrodialysers for the preparation of acids and alkalis or for other chemical reactions with participation of hydrogen and hydroxide ions. The decomposition of water in such systems is the "working" process and the efficiency of the entire electromembrane technology depends on the overpotential and current yield with which the H^+ and OH^- ions are generated.[5,6] The joint demineralisation and preparation of acid and alkali can be achieved in the so-called "semidipolar" membranes,[7–9] which are obtained by depositing a unipolar cation or anion exchanger on the membrane and also by the coprecipitation of the ion exchanger and polyelectrolyte.

Secondly, the problem of the intensification of the mass transfer in membrane systems has come to the fore and the applications of electrodialysis have been extended to the preparation of deionised or ultrapure water. The electrodiffusion process is then carried out under postlimiting conditions (the current is greater than the limiting diffusion current), where water decomposes very quickly and this process itself can intensity the mass transfer of electrolyte across membranes[10,11] by increasing the electrolyte concentration in the region of the diffusion layer near the membrane and by increasing thereby the migration current (the so called "current exaltation effect"). Finally, there has been a growth of interest in the role which the transport of H^+ ions across biological membranes plays, especially in photosynthetic processes,[12,13] where local electric fields in membranes initiate the heterolytic cleavage of water molecules and the injection of H^+ into the membrane.

II. DISSOCIATION OF WATER MOLECULES AT THE MEMBRANE–SOLUTION BOUNDARY

The possibility of the dissociation of water when an electric current is passed through ion-exchange membranes was established a long time ago. As early as 1914, Bete and Toropoff[14] observed the transport of water dissociation products through certain membranes (gelatin, parchment, and collodion membranes). The involvement of H^+ and OH^- ions in transport across ion-exchange membranes was observed in 1946 by Frilette[15] and independently by Kressman and Tye[16] and was later confirmed by many workers.[17–27]

It has now been established reliably that the rate of decomposition of water and the fluxes of H^+ and OH^- ions in the membrane system depend greatly on the nature of the ionogenic groups.[11,19–24,28–30]

† This article was planned for publication in issue No.6 (1988) of this journal, which was devoted to the problem of polymer membranes.

For cation-exchange membranes at currents exceeding the limiting current by a factor of 1.5–2, the change in the pH of the solutions near the membrane is insignificant[31] and the transport numbers of the H^+ ions are in the range from 4×10^{-5} to 0.11.[4,18,26,29,32,33] On the other hand, the transport of OH^- ions across anion-exchange membranes takes place at a much higher rate and the transport numbers reach 0.03–0.6.[4,17-19,26,29,32-36]

Since the concentrations of H^+ and OH^- ions in the spontaneous decomposition of water molecules in water are identical, while the mobility of H^+ ions in ion-exchange resins is greater than that of OH^-, this finding is in conflict with the usual ideas about the electrodiffusion character of the transport of ions across membranes. Many workers therefore assumed that the transport of H^+ ions across a cation-exchange membrane is suppressed by some factor and they introduced the additional hypothesis that the states of the interfaces at the cation-exchange and anion-exchange membranes are different. Thus it has been postulated[37,38] that, at high current densities, an intense flux of electrolyte ions induces the partial disruption of the diffusion layer. The effect of the disruption of this layer is greater on the side of the cations, since they are more hydrated. This results in the appearance of additional possibilities for increasing the electrolyte flux, while the transport of H^+ ions across the cation-exchange membrane is suppressed.

Similar ideas were developed in other studies.[15,33,34,39] The decomposition of the diffusion layer has been attributed[15] to the establishment of electro-osmotic fluxes on the surface of the membrane owing to its inhomogeneity, while other workers[33,34,39] attributed it to the appearance of local convective currents near the interface as a consequence of the evolution of joule heat in the desalinated layer of solution. By applying the schlieren method and photography with the aid of Toepler's apparatus, Varentsov and Pevnitskaya[34] confirmed experimentally that the local thermoconvection arises at a cation-exchange membrane for electric currents exceeding the limiting diffusion current, while at an anion-exchange membrane this effect is very weak. The results obtained were explained by the different degrees of hydration of anions and cations (Mandersloot's mechanism[37,38]) and also by the existence on the surface of anion-exchange membranes of films with a low concentration of fixed groups.[33,34,39] Kononov and Vrevskii[4] explain the preferential transport of OH^- ions across anion-exchange membranes by their high selectivity with respect to hydroxide ions. After converting the membranes from the salt to the hydroxide-forms, they observed an increase in the rate of dissociation of water. Measurement of the electrolyte concentration at the interface using the commutator method (the current interruption method) made it possible to establish[18] that, at currents close to the limiting diffusion current, the limiting electrolyte concentration near the cation-exchange membrane does not attain low values comparable to the concentrations of the H^+ and OH^- ions in water, while at an anion-exchange membrane they are attained readily. Subsequently these results were confirmed in a study[40] using analogous methods and in other investigations[41–44] in which modern direct methods for recording electrolyte concentrations with the aid of laser holography were employed.

The earlier conclusions[34,39] that local convection arises in the solution at the surface of a cation-exchange membrane were confirmed and specified in greater detail by the methods of laser holographic interferometry[41,43,45] and also by measuring the electrochemical noise in membrane systems.[46–50] At currents only slightly exceeding the limiting current, the convective streams are laminar in character and do not influence the electrical resistance of membrane systems.[48] When the limiting current is exceeded by a factor of three, laminar convection is converted into turbulent convection, causing random oscillations in the resistance of the desalinated layer of solution, which is manifested by the appearance of flicker noise.[48] After the attainment of the turbulent thermoconvection regime, the electrical resistance of the membrane system falls.[48] By an additional series of elegant experiments, the authors[48] demonstrated that the convective currents generated obey known laws: with increase in the viscosity of the system by the addition of a non-ionisable water-soluble polymer, with decrease in the temperature of the solution, or for the horizontal disposition of the cation-exchange membrane (the desalinated layer of the solutions lies below), the noise induced by convection weakens. The frequency-independent "white" noise, associated with the water dissociation reaction, is not observed in a system with a cation-exchange membrane.[47]

On the other hand, convective currents in the desalinated layer of solution have not been observed at an anion-exchange membrane for currents close to the limiting value either from the form of the interferograms[45] or by analysing the frequency spectrum of the noise[47,49] but the "white" noise has been distinctly observed, indicating the decomposition of water. With increase in the current, the intensity of the "white" noise increased linearly and, after the attainment of the limiting current, it began to grow faster than predicted by a linear law.[49] Only at very low current densities, exceeding the limiting current by a factor greater than three, does a weak flicker noise appear for an anion-exchange membrane, indicating the occurrence of thermoconvection.

Quantitative allowance for thermoconvection in a rigorous description of electrodiffusion is a complex task and involves many difficulties already in the stage of its formulation. Theoretically, thermoconvection can be taken into account indirectly by assuming that the electrolyte concentration at the interface does not diminish below a certain value as a result of thermoconvection. Here it has been shown[51] that, instead of a horizontal plateau on the voltage–current plot, a section corresponding to a retarded growth of current with increasing potential appears.

The reason for the different behaviour of cation-exchange and anion-exchange membranes has not been elucidated.[44–50] It also remains obscure why thermoconvection is observed near a cation-exchange membrane but not near an anion-exchange membrane, although, it follows from results of these workers and those of other investigators[18,40,43] that the boundary electrolyte concentration near an anion-exchange membrane in the limiting state is lower than near a cation-exchange membrane and that the liberation of joule heat because of this should be more intense near an anion-exchange membrane.

In our view, the appearance of thermoconvection and the consequent growth of the concentration of the counterions at the cation exchanger–solution interface are a consequence and not the cause of the low rate of decomposition of water. In fact, the dissociation of water, which occurs with a large negative heat change (the enthalpy of dissociation of water is 56.6 kJ mol^{-1} [52]), compensates for the liberation of joule heat on passage of the current through the highly desalinated layer of solution at the interface, so that thermoconvection is very significant near an anion-exchange membrane, while the concentration of counterions diminishes to values comparable to the concentrations of H^+ and OH^- ions.[18,40,43,44,53] Around a cation-exchange membrane, the endothermic water dissociation process takes place at a very low rate and the passage of current therefore causes local heating of the solution at the interface and intense thermoconvection with all the consequences arising from it.

This approach explains the differences in the hydrodynamic state of the interfaces of cation-exchange and anion-exchange membranes observed in practice but leaves open the question of the causes of the different rates of decomposition of water at these membranes. The solution of this problem requires primarily the elucidation of the characteristic features of the mechanism of the dissociation of water in membrane systems.

If it is assumed that in a membrane system water decomposes at the same rate as in the usual aqueous solutions (the dissociation rate constant is $k_d = 2.5 \times 10^{-5}$ s^{-1} [54]) and the concept of the reaction layer is used,[55] the current transported by the H^+ and OH^- ions across the membrane (i_w) can be expressed in terms of the rate constants for the forward (k_d) and reverse (k_r) reactions, the concentrations of water (c_{H_2O}) and H^+ and OH^- ions (c_H and c_{OH} respectively), and the thickness of the reaction layer (λ):

$$i_w = F\int_0^{\lambda}(k_d c_{H_2O} - k_r c_H c_{OH})\,dx \leqslant F k_d c_{H_2O}\lambda. \qquad (1)$$

As can be seen from Eqn.(1), the partial electric current involving hydrogen or hydroxide ions (i_w) has an upper limit: under stationary conditions, the fluxes of H^+ and OH^- ions across membranes cannot be greater than the rate of formation of these ions in the reaction layer and the latter quantity is limited by the values of k_d and λ. The upper limit to i_w has been estimated[35,36] as 2×10^{-4} A m^{-2} at 25 °C, i.e. it is 10^7 times smaller than the current due to H^+ and OH^- ions actually observed in membrane systems.

Despite the approximate character of these estimates (the approach adopted by Simons and co-workers[35,56] is strictly applicable only in the presence of a supporting electrolyte when the electromigration transport of the ions formed in the reaction can be neglected[55]), a marked inconsistency is observed between the results of the calculation and the real rates. Even allowance for the electromigration ion transport[57] does not greatly improve the estimate.[36] The high rates of dissociation of water in the membrane–solution system cannot be explained from the standpoint of the Wien effect for weak electrolytes. The strength of the electric field arising in the region of the membrane–solution boundary is too low and the rate constant for the dissociation of water hardly differs from its value in the absence of the field.[58] The very fact of the decomposition of water and of the transport of H^+ and OH^- ions at the experimentally observed rates is therefore surprising and requires explanation, and not the ability of cation-exchange membranes to "suppress" the dissociation of water.[15,34,37–39]

The low limiting kinetic current for the water dissociation reaction in solution and marked dependence of the transport numbers of the H^+ and OH^- ions on the nature of the ion-exchange membranes lead to the conclusion that the cause of the high rate of this process should be sought not in the properties of the solution but in the characteristic features of the ion-exchange membranes.

As already mentioned, the rate of dissociation of water at cation-exchange (sulphonic acid) membranes in solutions of alkali metal salts is very low even when the actual current exceeds the limiting diffusion current by a large factor. However, as shown for the first time by Oda and Yawataya,[20] the dissociation of water increases sharply in this system when alkali metal cations are replaced by the Ca^{2+}, Mg^{2+}, and NH_4^+ cations. This effect was observed in the electrodialysis of sea water.[50] Subsequently it was established[60] that also certain other cations of weakly dissociating bases (Ni^{2+}, Co^{2+}, Mn^{2+}) are able to accelerate the decomposition of water, the reaction being accelerated not by the above ions themselves but by their hydroxides which are deposited on the surfaces of the membranes in electrodialysis and under postlimiting conditions are deposited especially on the surface of the cation-exchange membrane. The compounds $Cu(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$, and $MnCO_3$ also exhibit a catalytic activity. On the other hand, deposits of the compounds $Zn(OH)_2$, $CaSO_4$, $BaSO_4$, and $CaCO_3$ on the surface of the cation-exchange membrane do not influence the rate of decomposition of water.[60] This shows that the diffusion-dependent obstacles to the transport of electrolyte across the solid phase of the deposit on the membrane surface and the associated additional concentration polarisation are not the causes of the intensification of the dissociation of water.

The observed acceleration can be explained (at least qualitatively) by assuming that certain weakly dissociating substances are involved directly in the dissociation of water, for example, in accordance with the scheme

$$Mg(OH)_2 \rightleftarrows MgOH^+ + OH^-\,,$$
$$MgOH^+ + 2H_2O \rightleftarrows (MgOH)_2 + H_3O^+\,.$$

The rate constant for the heterolytic decomposition of water on groups of the type of $MgOH^+$ can be higher by several orders of magnitude than the rate constant for the non-catalytic reaction; the reaction can also be accelerated by the electric field at the deposit–membrane interface, where the space charge is localised. According to the data of Tanaka and Seno,[60] the formation of the deposits on the boundary between the membrane and the diffusion layer, which serves as the recipient of the counter ions, fails to influence the rate of decomposition of water in all cases.

In principle, the simple cations of weakly dissociating bases can also possess catalytic activity, for example, as a result of their participation in the reactions[36]

$$Mg^{2+} + 4H_2O \rightleftarrows Mg(OH)_2 + 2H_3O^+\,. \qquad (2)$$

$$Mg(OH)_2 \rightleftarrows Mg^{2+} + 2OH^-\,. \qquad (3)$$

The detailed mechanism of the dissociation of water in solutions with catalytically active inorganic ions is obscure as yet; the studies carried out hitherto on this question[20,59,60] have been qualitative. In particular, the claim by Tanaka and Seno[60] that the acceleration of the water dissociation reaction takes place in all cases only after the formation of the solid phase of the deposit, is incomprehensible and requires additional experimental confirmation. From the standpoint of Simon's scheme[36] [Eqns.(2) and (3)], the acceleration can be promoted by catalytically active cations of the type of Mg^{2+} present in the double layer at the membrane–solution interface, while the presence of the solid phase of the insoluble compound is not obligatory.

It has been shown[25,35,36] that the dissociation of water can be accelerated by certain organic bases B and acids AH, in particular compounds with tertiary amino-groups:

$$B + H_2O \rightleftarrows BH^+ + OH^-\,, \qquad (4)$$

$$BH^+ + H_2O \rightleftarrows B + H_3O^+\,, \qquad (5)$$

$$A^- + H_2O \rightleftarrows AH + OH^-\,, \qquad (6)$$

$$AH + H_2O \rightleftarrows A^- + H_3O^+\,, \qquad (7)$$

and that the dissociation can be accelerated both by the groups contained in the membrane[25] and introduced into the solution.[36] Having compared, in terms of the reaction layer approximation, the rates of decomposition of water in the catalytic reaction [Eqns.(4) to (7)] and the usual reaction

$$H_2O \rightleftarrows H^+ + OH^- \qquad (8)$$

Simons[36] showed that the acceleration of the reaction as a result of catalysis by organic substances can be very great.

In a number of studies, the description of the voltage–current plots for membrane systems by the authors assumes a local equilibrium in the water dissociation reaction at all points within the system,[61,62] which is equivalent to considering the reaction as "rapid". Despite the controversial nature of this assumption, Zholkovskii and co-workers[61,62] were able to describe qualitatively the shape of the voltage–current plots.

III. DISSOCIATION OF WATER MOLECULES IN DIPOLAR MEMBRANES

The term dipolar ion-exchange membranes is applied to layered membranes consisting of at least one cation-exchange and one anion-exchange layer which are in contact. In an electric field, dipolar membranes are arranged in such a way that the layers represent series-connected resistances in relation to the electric current passing through the system. If the cation-exchange layer is directed towards the cathode and the anion-exchange layer towards the anode, then, on passing of the electric current, the electrolyte concentration in the region of contact between the layers diminishes and, from a certain instant, the H^+ and OH^- ions formed in this region on dissociation of water are included in the transport process.

The dipolar membranes operating under conditions involving the generation of H^+ and OH^- ions have undoubted advantages over the membrane–solution system from the standpoint of the possibility of investigating the dissociation of water. Instead of the diffusion layer, which arises, for example, near a cation-exchange membrane, in a dipolar membrane there exists an anion-exchange layer which suppresses the influence of convection in solution, is selective with respect to anions, and thereby diminishes the transport of cations. This results in a high current yield of the H^+ and OH^- ions, reaching 0.9–0.96.[63] Furthermore, more reproducible data have been obtained at dipolar membranes than in a membrane–solution system.

The high current densities with respect to H^+ and OH^- ions, reaching 10^3 A m^{-2}, are a unique feature of dipolar membranes.[64] This exceeds by many orders of magnitude the limiting kinetic current for the water dissociation reaction [Eqn.(1)]. For a long time no attention was paid to this paradox and the water dissociation reaction was regarded as rapid[65] without any explanation.

Greben' et al.[66] were the first to point out the important role of the ionogenic groups in the dissociation of water, having assumed that the ionogenic group can participate directly in the reaction, accelerating it. They investigated by the voltammetric method dipolar membranes containing sulphonic, carboxylic, and phosphonic acid groups and concluded that the decrease in the potential differences in the membranes in the sequence

$$-SO_3H > -COOH > -PO(OH)_2$$

can be explained by the decrease of the energy barrier to the interaction of the ionogenic groups with water molecules as the pK of the cation-exchange groups increase in the same sequence.

The available quantitative information about the dissociation of water in dipolar membranes[67–74] includes voltage–current plots for the dipolar region, which are inaccessible to direct d.c. measurements, the effective dissociation and recombination rate constants, and equilibrium constants. The authors of the above studies used for the investigation of dipolar membranes the method of the frequency spectrum of the electrochemical impedance[67] with simultaneous polarisation of the membranes with a direct current. Analysis of the frequency spectrum made it possible to isolate from the overall impedance its component which refers to the dipolar region[69] and to calculate the effective reaction constants.[68] The mechanism of the dissociation, postulated in the calculations, does not take into account the role of the ionogenic groups in the reaction; as a result of this, the calculated constants are merely effective quantities. Nevertheless, this approach made it possible to compare the properties of dipolar membranes differing from one another by the nature of the ionogenic groups.[74]

The brands of the dipolar membranes and of the cation- and anion-exchange resins used for this preparation.[75]

No.	Brand			No.	Brand		
	of dipolar membrane	of cation-exchange resin	of anion-exchange resin		of dipolar membrane	of cation-exchange resin	of anion-exchange resin
1	MB-4	KF-1	AV-23M	6	MB-51	SG-1	AV-17
2	MB-31	KF-1	EDE-10P	7	MB-6	KU-2	AN-22
3	MB-3	KF-1	AV-17	8	MB-1	KU-2	EDE-10P
4	MB-42	SG-1	AV-23M	9	MB-2	KU-2	AV-17
5	MB-13	SG-1	EDE-10P				

Note. The brand names of the industrial MB-1, MB-2, MB-3, and MB-4 membranes are as given in a catalogue (Ref.75, p.15). The MB-2 membrane has been alkylated with methyl iodide.[70] The remaining membranes are experimental (conventional brand names) and have been prepared at the "Plastmassy" [Plastics] NPO.

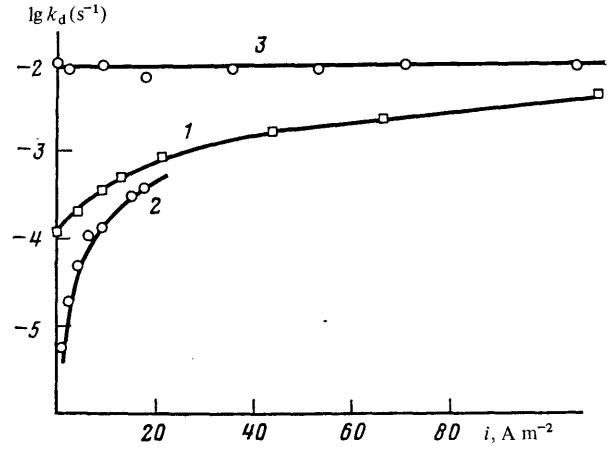


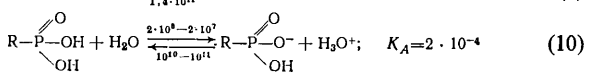
Figure 1. Dependence of the rate constants for the dissociation of water in the dipolar region of MB-1 (curve *1*) and MB-2 (curve *2*) membranes at 25 °C and the MB-3 membrane (curve *3*) at 4 °C on the current density. The logarithm of the rate constant for the dissociation of water is -4.6 at 25 °C and -5.5 at 4 °C.[72]

The rate constants for the dissociation of water in dipolar membranes (the bands of the membranes are indicated in the Table) differ sharply from the corresponding constants for the same reaction in pure water (Fig.1); they depend on the nature of the ionogenic group and the current density. Phosphonic acid groups have

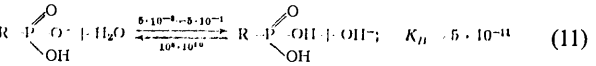
such a marked catalytic effect that the increase in the reaction rate constant due to the electric field applied to the membrane from outside cannot be seen against this background (Fig.1, curve *3*). At low current densities, sulphonic acid groups hardly accelerate the dissociation (Fig.1, curve *2*) and the rate constant is in this case almost the same as in pure water. At high current densities, the constant increases, the field effect predominating under these conditions. The involvement of the tertiary amino-groups in the dissociation of water in dipolar membranes has been confirmed:[70] the alkylation of tertiary amino-groups of the dipole membrane sharply increases the overpotential and decreases the rate constant for the dissociation of water. This effect also shows that sulphonic acid groups have a significantly weaker catalytic activity than the tertiary amino-groups.

The extremely low overpotential in the dipolar region of the membranes containing phosphonic acid groups can be explained from the standpoint of the catalytic mechanism.[71] Calculation showed[72] that, among all the possible water dissociation reactions in these membranes

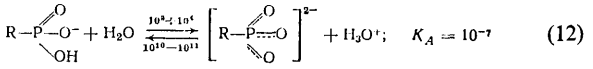
$$H_2O + H_2O \underset{1,4\cdot10^{11}}{\overset{2,5\cdot10^{-5}}{\rightleftharpoons}} H_3O^+ + OH^-; \quad K = 1,8\cdot10^{-16} \qquad (9)$$



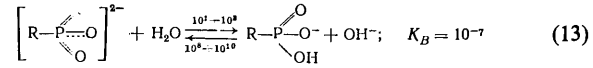
(10)



(11)



(12)



(13)

(the rate constants, in s^{-1} expressed for the forward reaction and in litre $mole^{-1}$ s^{-1} for the reverse reaction, are indicated above and below the arrows; the equilibrium constants, in mole $litre^{-1}$, are indicated after the reactions), the last two make the main contribution. In order to ensure the dissociation of water, reactions (10) and (11) or (12) and (13) (or both pairs simultaneously) must take place consecutively in the forward direction. In each pair of reactions, the rate of dissociation is limited by the stage with the lowest rate constant [stages (11) and (13)]. Since both pairs of reactions can take place simultaneously, and the rate constant for stage (13) in the forward direction is greater by a factor of 2×10^3 than the rate constant for stage (11), reactions (12) and (13) make the greatest contribution to the dissociation.

The catalytic mechanism of the dissociation of water in dipolar membranes is confirmed by the dependence of the rate constant for the rate-limiting stage of the dissociation of water, found for reactions (9)–(13), on the effective equilibrium constant for the dissociation calculated from the impedance frequency spectra (Fig.2). In terms of the catalytic effectiveness, the ionogenic groups of dipolar membranes can be arranged in a sequence in order of increasing rate constants for the dissociation of water involving their participation:[74]

	$-N(CH_3)_3$	$<$	$-SO_3H$	$<$	$-PO_3H^-$	$<$	$=NH$,	$-NH_2$	$<$	$\equiv N$	$<$	$-COO^-$	$<$	$-PO_3^{2-}$
k (s^{-1})	0		$3\cdot10^{-3}$		$3\cdot10^{-2}$		10^{-1}			1		10		10^3

The dependence of the activation energy for the dissociation of water on the nature of the ionogenic groups (Fig.3) is important evidence in support of the catalytic mechanism for the dissociation of water in dipolar membranes. The activation energy for membranes with a weak catalytic effect (MB-1 membrane, 45 kJ mol^{-1}) is close to the activation energy in pure water (56 kJ mol^{-1}), while phosphonic acid groups reduce sharply this quantity (MB-3 membrane, 26 kJ mol^{-1}). The low activation energies for the MB-2 membrane (32.5 kJ mol^{-1}) are associated with the pronounced heating of its dipolar region.[77]

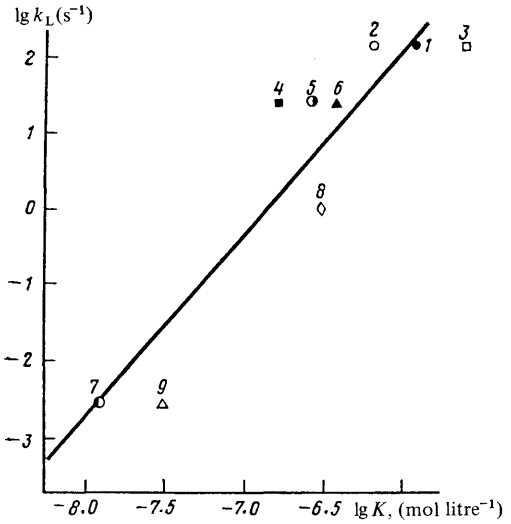


Figure 2. Dependence of the rate constant for the rate-limiting stage (k_L) of the dissociation of water on the effective equilibrium constant of the water dissociation reaction calculated from the impedance frequence spectra.[74] The numerals opposite the symbols correspond to the numbers of the membranes in the Table.

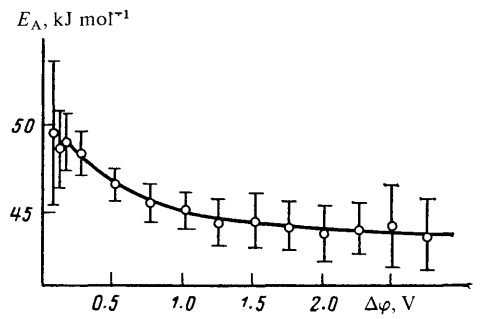


Figure 3. Dependence of the activation energy for the dissociation of water in the MB-1 membrane[69] on the overpotential of the dipolar region. The activation energy for the dissociation reaction is 56 kJ mol^{-1} in pure water,[76] 32.5 kJ mol^{-1} in the MB-2 dipolar membrane,[66] and 26 kJ mol^{-1} in the MB-3 membrane.[66]

The dissociation of water in the dipolar region takes place under conditions different from those in pure water or in aqueous solutions. This is associated not only with the presence of the polymer

matrix, the fixed ionogenic groups, and counterions but also with the presence of electrical double layer at the site of contact between the cation exchanger and the anion exchanger.[78] Within the limits of this layer, the concentration of both the counterions and co-ions is low compared with the concentration of the fixed ions and this region has come to be called the "exhausted" layer.

There are at least three causes of the increase in the rate of dissociation of water in the exhausted layer. Firstly, the decrease in the concentration of the H^+ and OH^- ions in the exhausted layer increases the degree of dissociation of the ionogenic groups, and hence also the concentrations of the charged forms, and increases the rates of the proton transport reactions in which they participate.[79] The second cause is associated with the polarisation of the H—OH bond by the electric field of the ionogenic group and also by the external electric field applied to the exhausted layer:[80–84]

$$k_d = k_d(0)\exp\left(\beta E + \frac{\alpha FE}{RT}\right) ,$$

where k_d is the rate constant for the heterolytic dissociation of water molecules in an electric field with a strength E, $k_d(0)$ is the corresponding constant in the absence of the field, and α and β are parameters taking into account respectively the decrease in the activation energy for the dissociation of water in the electric field and the entropy effect accompanying the orientation of water molecules in the vicinity of the ionogenic group and its dissociation. Thirdly, the dependence of the rate of dissociation of water molecules on the potential applied to the membrane is due to the expansion of the region of the space charge where dissociation actually occurs.

The dependence of the rate constant for the dissociation of water on the electric field strength, predicted by the Onsager theory for the second Wien effect, has been used in a number of studies for the description of processes in dipolar membranes.[85–87] Despite the qualitative agreement with experiment, from the standpoint of these ideas, it is difficult to explain the marked dependence of the properties of the membranes on the nature of the ionogenic groups. The same difficulty arises when one uses the model of the "neutral" layer, which is assumed to exist btween the cation exchanger and the anion exchanger in the dipolar region.[56] For certain membranes with an increased electrical resistance, it is essential to take into account the increase in the rate constants for the dissociation of water owing to the heating of those membranes at high current densities.[77]

It is noteworthy that all the approaches used to describe the dissociation of water in dipolar membranes and the models of such membranes[56,81,85] are mutually exclusive, although each investigator has found good agreement when comparing his model with experiment.

Comparison of the known models for the dissociation of water in dipolar membranes with experiment has demonstrated that the model of Timashev and Kirganova[81] agrees with the experimental data in terms of the largest number of criteria. Unfortunately, the accuracy of the experimental data (the voltage—current plots, the impedance frequency spectra) does not at present make it possible to determine all the constants for the space charge region and the water dissociation reaction.

Thus the best model of the dipolar membrane under the conditions corresponding to the generation of H^+ and OH^- ions, which takes into account the non-equilibrium nature of the processes occurring in the space charge region, is that proposed by Timashev and co-workers.[81–83] The ideas developed in these studies agree fully with the catalytic mechanism of the water dissociation reaction at the ionic groups of the membranes.

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One can now regard it as a reliably established fact that the dissociation of water molecules in membrane systems takes place preferentially in the regions of the localisation of the space charge in the membrane phase with active participation of the ionogenic groups. In membrane systems lacking catalytically active groups, the dissociation of water takes place via the usual mechanism as a non-catalytic homogeneous reaction. In order to intensify the dissociation of water in membrane systems, catalytically active groups can be introduced both into the polymer matrix of the membrane and into the solution around the membrane.

Further progress in the study of the water dissociation reaction in membrane systems is related to the need to examine the elementary processes occurring with participation of catalytic centres in the space charge regions and the interfaces. The knowledge of the characteristic features of the water dissociation reaction in such systems will make it possible to alter specifically the surface properties of the membranes in order to facilitate or suppress this reaction. The dissociation of water must be taken into account in a theoretical description of membrane systems and in the planning and operation of electromembrane apparatus.

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Interaction of Refractory Metal Oxides with Carbon

A.G.Vodop'yanov, G.N.Kozhevnikov, and S.V.Baranov

Certain characteristics of carbothermal processes involving the reduction of refractory oxides to the metal are surveyed with allowance for the structure of the outer and penultimate electron shells. The similarity and difference between the kinetics and mechanisms of reactions on the surfaces of the metal oxides and the carbon reductant are analysed.
The bibliography includes 147 references.

CONTENTS

I. Introduction 810
II. Thermodynamics of carbothermal reduction processes 810
III. Chemical adsorption of carbon monoxide on metal oxides 811
IV. Reactions involving the reduction of refractory oxides to the metals 812
V. Oxidation reactions of solid carbon 818

I. INTRODUCTION

The interaction of refractory metal oxides with carbon constitutes the basis of many metallurgical processes and of the technology for the preparation of materials for high-temperature engineering. The complexity of the mechanisms of these processes is due to the wide variety of the physicochemical properties of the elements formed in the reduction process and of their compounds. For this reason, carbothermal processes involving reduction to the metals have been the subject of continuous investigations and attempts to create a unique theory[1-10] from the standpoint of which it will be possible to predict and explain the role of the individual components of the reduction reactions.

The various views which have arisen hitherto concerning the mechanism of carbothermal reduction to the metals are related to the appearance of new promising trends in chemistry and to the employment of the advances achieved in them. Thus the application of the thermodynamic analysis to the study of metallurgical process has served as a basis for the development of ideas concerning the leading role of oxide dissociation reactions,[11] the development of catalysis led to the adsorption-autocatalytic theory,[1] studies on the evaporation and dissociation of substances led to the discovery of the oxide-sublimation mechanism of the reduction process,[4] mass-spectrometric detection of short-lived oxygen–carbon compounds demonstrated the active role of C_2O_5 as a reductant,[9,12] and the use of atomic-absorption analysis led to the discovery of the gas-carbide reduction mechanism.[13,14]

All these ideas reflect to different extents the phenomena observed in the study of reduction processes. As a result, many investigators have now adopted the view[4,5,9,12,15] that the mechanism of carbothermal reduction to the metals cannot be described from the standpoint of any single universal theory. This view is correct. However, it does not rule out the possibility of establishing general characteristics of the reduction of different groups of oxides having similar physicochemical properties (Ref.4, p.269).

The present review surveys data which have accumulated during the last decade on the high-temperature chemisorption of gases and the thermodynamics, kinetics, and mechanisms of the interactions of solid oxides of refractory metals with carbon. These processes take place simultaneously on the surfaces of both reactants and for this reason in the systematic treatment of the results the reduction process has been divided into two classes of reactions occurring on the surfaces of metal oxides and carbon reductants.

The characteristics of the variation of the properties of chemical compounds (including metal oxides) on passing from one compound to another are associated with the properties of the individual atoms. In order to elucidate the features of the kinetics and mechanisms of carbothermal reduction processes, it is therefore useful to examine the accumulated data with allowance for studies in the field of the systematic treatment of the elements.[16-19] The new version of the Periodic System of the elements[19] takes into account not only the limiting number of valence electrons but also the force characteristics of the latter, which are determined by the structure of the outer and penultimate electron shells. Together with group and type analogues of the elements, two new types of analogues have been differentiated in addition:[19] the shell analogues, i.e. those which not only refer to one subgroup but also have isotypical non-kinosymmetrical electron shells (for example, Ca–Sr–Ba, Zr–Hf, Y–Lu, etc.) and the shrink analogues—pairs of elements one of which (with the larger atomic number) has an orbital radius similar to or smaller than that of the preceding type analogue in the given group as a consequence of the *p*, *d*, or *f* contraction (for example, Ba–Ra, Si–Ge, etc.). The maximum similarity between the properties of certain elements has in fact been explained by their belonging to shell and shrink analogues.[19]

II. THERMODYNAMICS OF CARBOTHERMAL REDUCTION PROCESSES

Until recently, the method for the estimation of the probabilities of particular isolated reactions based on a comparison of their Gibbs free energies at the corresponding temperatures was widely used in the theoretical study of reduction processes. However, real reduction processes represent a set of interlinked reactions, which must be taken into account as an assembly of reactions.

Methods for the construction of phase and chemical equilibrium diagrams[20,21] and thermodynamic balances,[22] involving the solution of a system of equations for the equilibrium constants of the corresponding reactions under the conditions of a congruent transition

of the chemical compound from the condensed to the gaseous state, are used for this purpose.[8,23-25] On the basis of this approach, the carbothermal reduction process is represented by a set of reactions involving the dissociation of metal oxides and molecular oxygen to the constituent gaseous elements, the oxidation of CO to CO_2 by oxygen, and the regeneration of CO by solid by solid carbon.[26] The solution of the system of equations for the equilibrium constants of these reactions at a fixed CO pressure makes it possible to estimate the composition of the gas phase under conditions where the metal oxide is in equilibrium with the $O-O_2-CO-CO_2$ gas phase, which is in its turn in equilibrium with solid carbon. The equilibrium compositions of the gas phase in the interaction of SiO_2,[27] Al_2O_3,[28] Group IIA metal oxides,[29,30] and MnO [31] with carbon have been calculated by a similar method.

In the study of reduction processes in multicomponent systems, computer programs for thermodynamic calculations have been used in recent years.[32-36] Theoretical studies of the equilibrium compositions of condensed and gaseous phases in the interaction in the Si–O–C,[37,40] Al–Si–O–C,[41] Al–O–C,[10,42] Ti–O–C,[43,44] Nb–O–C,[45-48] Zr–O–C,[43] Ce–O–C,[49] and Nd–O–C [10] systems have been carried out by these methods.

A decrease in pressure in these systems promotes the development of reduction processes with lower temperatures and intensifies the tendency towards decomposition of the condensed reduction products—towards the transfer of the substance to the gas phase.

The accumulated results of thermodynamic studies have shown that, under equilibrium conditions, the main gaseous reduction product is CO. The pressure of the remaining carbon oxides C_2O, CO_2, and C_3O_2 as well as the C, C_2, C_3, O, O_2, and O_3 components is more than 5 orders of magnitude smaller than the CO pressure. At pressures close to 0.1 MPa, the reduction of oxides to *s* and *sp* elements (BeO, MgO, CaO, SrO, BaO, SiO_2, and Al_2O_3) and MnO is accompanied by the formation in the gas phase of the vapours of the metals and their lower oxides as the reduction products. On the other hand, the reduction of oxides to the *d* and *f* elements (TiO_2, Nb_2O_5, ZrO_2, Ce_2O_3, and Nd_2O_3) is characterised by very low concentrations of the metal-containing reduction products in the gas phase. An increase in their concentration in these systems is observed only at high temperatures or as a consequence of the thermal decomposition of the intermediate compounds, in particular metal carbides.

The low equilibrium concentration of CO_2 in systems with metal oxides which are difficult to reduce does not provide grounds for the conclusion that it plays an insignificant role in reduction processes. However small the equilibrium CO_2 pressure, the probability of the interaction of metal oxides with CO in the presence of solid carbon increases at the temperatures where the carbon gasification reaction ensures an equilibrium CO_2 pressure lower than in an isolated reaction involving reduction with carbon monoxide.

Thus, in terms of the composition of the components of the equilibrium gas phase, the interactions of refractory metal oxides with carbon at pressures close to 0.1 MPa can be divided into two groups differing in the content of the vapours of metals and their lower oxides. The difference between them is correlated with the structure of the outer and pre-outer electron shells of the elements produced by the reduction process. The first group includes processes involving reduction to the *d* and *f* elements with the preferential formation of CO and the second involves the reduction of oxides to *s* and *sp* elements and manganese (from MnO) with the additional formation of the vapours of metals and their lower oxides.

III. CHEMICAL ADSORPTION OF CARBON MONOXIDE ON METAL OXIDES

The chemical adsorption of CO on the surfaces of metal oxides is not only one of the intermediate stages in the carbothermal reduction process but it also has independent importance in processes involving the catalytic oxidation of CO and the purification of exhaust gases. The results[50-53] which have accumulated in the field of heterogeneous catalysis and oxygen exchange involving metal oxides therefore make it possible to elucidate the mechanism of the chemical adsorption of CO and its role in high-temperature reduction processes.

The adsorption properties of metals and their oxides are determined to a large extent by their electrical properties and the participation of conduction electrons in the formation of complexes between the adsorbent and adsorbate. The higher their electrical conductivity, the greater their adsorption-catalytic capacity. In non-transition metal oxides, cations with outer s^2 and s^2p^6 electron shells are stable, because their electronic levels are not split by the atoms or molecules in the first coordination sphere. For this reason, the conductivity of the oxides of *s* and *sp* elements is very low. A similar stability of the electron shells of the cations has been observed also for transition metal oxides with ions having the configurations $d^0(Sc^{3+}, Ti^{4+}, V^{5+})$, $d^5(Mn^{2+}, Fe^{3+})$, and $d^{10}(Cu^+, Zn^{2+})$, which makes their catalytic properties similar to those of non-transition metal oxides.[54] The oxides of *d* transition metals, on the surfaces of which coordination-unsaturated cations with incomplete *d* orbitals (in which the number of electrons is not 5 or 10) are present, have the maximum catalytic activity. Such oxides are characterised by a higher crystal lattice energy than oxides with analogus ions having the s^2, s^2p^6, d^5, and d^{10} outer electrons. Lanthanide oxides with incomplete *f* orbitals (in which the number of electrons is not 7 or 14) also possess a considerable catalytic activity, for example, Nd_2O_3 [55] and ThO_2.[56] CO is adsorbed reversibly on zinc oxide at temperatures below 373 K.[53] At higher temperatures the adsorption is irreversible with formation of CO_2 molecules. Irreversible adsorption of CO has been recorded on the surfaces of Cr_2O_3, ZnO, CoO, and Mn_2O_3.[53] Under these conditions, the irreversibly adsorbed CO is bound to the surface of the metal oxide in the form of the "carbonate ion" CO_3^{2-}, which arises when CO interacts with the oxygen ions of the oxide lattice. On copper, cobalt, and nickel oxides, the adsorbed CO is capable of reacting not only with the oxygen of the oxide lattice but also with oxygen adsorbed on the oxide surface.

Depending on the temperature, the catalytic oxidation of CO on the surfaces of transition metal oxides proceeds via two mechanisms. At low temperatures it proceeds via an associative mechanism with formation of intermediate carbonate CO_3^{2-} structures,[57-59] which are decomposed by gaseous oxygen with formation of CO_2 molecules. With increase in temperature, the associative mechanism of the oxidation of CO passes to a multistage mechanism,[57-61] which is induced by the sharp decrease in the coverage of the metal oxide by surface carbonate ions and their rapid thermal decomposition with formation of CO_2 by reaction with the oxygen in the oxide lattice. The subsequent adsorption of oxygen from the gas phase leads to the disappearance of metal ions as the reduction products and to the formation of the radical-ions O_2^- on the surface of the metal oxide. As a result, the multistage mechanism represents alternate oxidation-reduction of the surface of the oxide catalyst. The temperature range corresponding to the change in the mechanism of the catalytic

oxidation of CO on oxides of metals in the Fourth Period (V_2O_5–ZnO) is 518–863 K,[60] while on TiO_2 this happens at 1173 K,[57] which is close to the temperatures of the onset of the surface diffusion of the metal oxide cations and anions.[62] In essence, the change of the mechanism of the catalytic oxidation of CO at high temperatures is induced by the involvement of reactions leading to reduction to the metal by the gaseous reductant.

The oxides of *s* and *sp* elements, which are dielectrics under normal conditions, exhibit the properties of semiconductors at high temperatures and low pressures.[63] As a result, conduction electrons, capable of participating in gas–adsorbent reactions, appear on their surfaces. Thus Group IIA metal oxides (BeO–BaO) and aluminium oxide (Al_2O_3) exhibit electronic conductivity at temperatures[63] close to the temperatures of the onset of appreciable interaction with carbon. A similar relation between the semiconducting nature of metal oxides and the temperature of the onset of interaction with carbon has been established in relation to the oxides V_2O_5, WO_3, and TiO_2.[4]

The isotope exchange observed in the study of the self-diffusion of oxygen in metal oxides[53] also indicates the occurrence of the high-temperature chemical adsorption of gases on the surfaces of metal oxides. The character of the adsorption of oxygen depends on temperature. At room temperature, oxygen is adsorbed in the molecular form, while at elevated temperatures it is adsorbed in various dissociatively adsorbed forms.[53]

The high-temperature isotope exchange of oxygen has been studied in the oxides SiO_2 [64] and Y_2O_3 [65] at 1123–1523 K and 1273–1773 K respectively. According to Finikov,[66] it is observed from 673 K to the melting point and in melts of oxygen-containing compounds. The mechanism of such reactions is based on the isotope exchange within a chemisorption complex of the type $M_x[O_nA-O_2]_y$, where M is the metal and A the element forming the anion in which O_2 combines with A via a chemisorption bond, and ^{18}O is redistributed in the exchange process between AO and O_2.

Thus, results accumulated in the field of the catalytic oxidation of CO indicate an important role for chemical adsorption of CO in processes involving the high-temperature reduction of refractory oxides. In contrast to the oxides of *d* and *f* transition metals, the CO chemisorption processes on non-transition metal oxides take place at very high temperatures, corresponding to the appearance of semiconducting properties in the oxides. It has been established[10] for the non-contact reaction of ZrO_2 with graphite at 2223–2323 K that, with increase in temperature, the intensity of the processes associated with the chemisorption of CO increases as a consequence of the increase in the number of active chemisorption centres formed owing to the increase in the concentration and mobility of the defects in the crystal lattices of the oxides.

IV. REACTIONS INVOLVING THE REDUCTION OF REFRACTORY OXIDES TO THE METALS

The interactions of metal oxides with carbon represent a definite class of chemical reactions whose common character and the differences between their properties are determined by the similarities and differences between the properties of the elements produced by the reduction process—the characteristic features of their variation as a function of the fundamental properties of atoms. Therefore the most common features of the kinetics and mechanisms of the high-temperature reduction processes in general and for individual groups of refractory metal oxides can be manifested in the analysis of the experimental data taking into account the distribution of the elements generated by reduction within the framework of the Periodic System.[18,19]

1. Reactions Involving Reduction to Group IIA Elements

The oxides of Group IIA metals interact with carbon to form a gas phase containing the vapours of the oxides and of the metals produced by reduction.[29,30,67–72] At p_{CO} = 0.1 MPa, the principal metal-containing component of the gas phase is the metal as the reduction product, whose partial pressure is higher by several orders of magnitude than that of the vapour of the corresponding metal oxide.[30] In the gaseous products of the reduction of barium oxide, the relative concentration of the oxide is somewhat higher than for the remaining group IIA metal oxides. With increase in temperature from 1773 to 2073 K, the fraction of BaO in the mixture of the metal-containing components of the gas phase diminishes from 26.09 to 5.73 vol.%.

The reduction on the surfaces of metal oxides without contact with the carbon reductant is accompanied by the formation of only gaseous products.[29,30] The highest average rate of reduction, referred to unit geometrical surface of the metal oxide, is observed at p_{CO} = 0.1 MPa. The decrease in the rate of reduction when CO is replaced by an inert gas indicates the leading role of CO as the reductant. The interaction of MgO, CaO, SrO, and BaO with carbon at p_{CO} = 0.1 MPa begins at an appreciable rate at ~1773 K and that of BeO begins at 2173 K. However, the carbides CaC_2, SrC_2, and BaC_2 are formed on carbon only at temperatures close to 2073, 1973, and 1923 K respectively when the partial pressure of the reduction-product metals, transferred from the surfaces of the oxides to solid carbon, exceeds the dissociation pressure of the corresponding carbide. The appearance of BeC_2 on solid carbon is possible only above 2560 K.[29,30]

Thus the metal formed on reduction in the presence of solid carbon can be either removed with the effluent gases or can react with the carbon to form the carbide depending on the conditions.

When the CO pressure is reduced from 0.1 to 3.4×10^{-6} MPa, the degree of conversion of the oxides BeO, MgO, and CaO increases (Fig.1), passing through a maximum close to $p_{CO} \simeq 4 \times 10^{-3}$ MPa.[10,29] The decrease in the CO pressure in the system favours an increase in the rate of diffusion and mass transfer between the reactants, which compensates for the decrease in the CO concentration in the range $p_{CO} = 4 \times 10^{-3}$–0.1 MPa. At p_{CO} less than 4×10^{-3} MPa, the contribution of the reactions involving reduction by carbon monoxide diminishes and the role of the oxide dissociation reactions, forming a vapour–gas phase consisting of the atomic metal, its monoxide, and molecular and atomic oxygen, is enhanced.[73] The rate of reduction on the surfaces of metal oxides *v* is correlated with the partial pressure of the metal produced by reduction[30,74] and with the Gibbs free energy ΔG_T^0 of the overall reduction reaction:[72]

$$MO(solid) + C(solid) = M(gas) + CO(gas),$$

which is expressed by the equation

$$\lg v = a - b\Delta G_T^0 \qquad (1)$$

where *a* and *b* are coefficients.

In contrast to BeO and MgO, whose rates of reaction with carbon obey individual relations, the rate of reduction of CaO, SrO, and BaO obeys a common numerical relation of type (1) determined by

the great similarity of the physicochemical properties of the corresponding metals as shell analogue Group IIA elements.[19]

Under conditions where CaO is in contact with CaC_2, a eutectic is formed, its fusion at a temperature above 2100 K leading to intense dissolution of CaO in the $CaO-CaC_2$ melt, a diminution of the role of the reduction reactions via the gas phase, and the preferential development of reduction reactions between the $CaO-CaC_2$ melt and solid carbon.[68] A similar change of mechanism is observed when barium is obtained by reduction at temperatures above 1923 K,[30] ensuring the formation of BaC_2 on carbon in the initial stage.

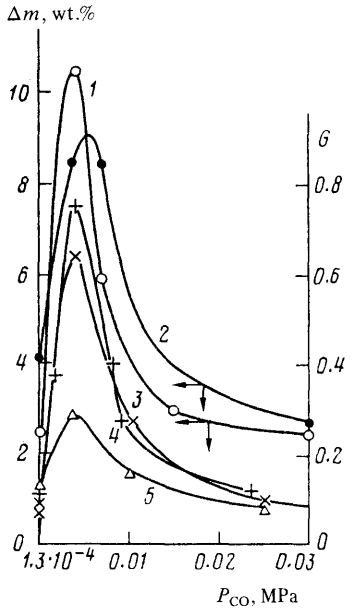


Figure 1. Decrease in the mass of metal oxides (Δm, wt.%) at a distance of 0.5 mm from graphite and in the degree of conversion of the oxides (G) in particulate mixtures with graphite as a function of the CO pressure: 1) Cr_2O_3 (1673 K); 2) CaO (2073 K); 3) SiO_2 (1773 K); 4) BeO (2223 K); 5) MgO (1873 K).[10]

2. Reduction to Aluminium

Among the oxides of Group IIIA elements, the most stable and refractory oxide is Al_2O_3. Its interaction with carbon takes place with formation of condensed (Al_3O_4, Al_4O_4C, Al_2OC, and Al_4C_3) and gaseous (Al, AlO, and Al_2O) products.[4,26,75] When Al_2O_3 was atomised in a graphite furnace, the presence of the carbide Al_2C_3 was detected together with aluminium in the gas phase by atomic-absorption analysis.[76-80] The ratios of the components of the gas phase ($c_{Al_2C_2}:c_{Al} = 10^2-10^3$) [77] calculated from the absorption spectrum of Al_2C_2 [13] conflict with the equilibrium concentrations of the components ($Al_2O_3:C:CO = 1:3:1$) [10] in the initial Al_2O_3-C systems[81] and with the results of the mass-spectrometric analysis of the evaporation products in the Al–C system.[82] According to the latter, $c_{Al}:c_{Al_2C_2} = 1050:1$. An analogous composition of the gas phase, mainly containing the metal vapour, has been observed in the mass-spectrometric analysis of the evaporation products of the carbides of *f* elements.[83] The results of the above studies[13,76-80] have been criticised[84] in a study where it was noted that the molecular spectrum obtained by L'vov and Ryabchuk[76] was arbitrarily attributed to the Al_2C_2 molecule (and not the AlC_2 molecule), while the estimate of the relative Al and Al_2C_2 concentrations, made on the assumption that the integral absorption coefficients of the corresponding atomic and molecular lines are similar,[13,79] is extremely inaccurate because the difference between the oscillator strengths even for atomic absorption lines can exceed 2–3 orders of magnitude. Therefore the concept of the gas-carbide reduction mechanism, which presupposes the transfer of carbon from the oxide surface by gaseous carbides of the type of MC_2 and its universal character regardless of the individual features of the oxide, experimental conditions, and the form of the products formed ultimately,[14] cannot be regarded as sufficiently well founded. Without contact between aluminium oxide and solid carbon at $p_{Ar} = 0.1$ MPa [85] and $p_{CO} = 0.1$ MPa,[28] condensed products (Al_4C_3) are formed on the surface of the reductant as a result of its interaction with the vapours of aluminium and its lower oxides.[86] The temperature of the onset of interaction at an appreciable rate is close to 2030 K at $p_{CO} = 0.1$ MPa,[28] at 1873 K at $p_{Ar} = 0.1$ MPa,[85] and at 1623 K in a high vacuum.[87] A decrease in the CO pressure from 0.1 to 3×10^{-6} MPa [10] promotes the acceleration of the reaction, which is particularly sharp at $p_{CO} < 4 \times 10^{-3}$ MPa (Fig.2).

When Al_2O_3 and the carbon reductant are in contact under conditions where $p_{Ar} = 0.1$ MPa,[85] reduction reactions through the gas phase proceed on the sections of the oxide surface free from contact with graphite, while at the sites of contact diffusional interaction occurs with formation of a $Al_2O_3-Al_4C_3$ solution. Ultimately the reaction of Al_2O_3 at the sites of contact with the reductant terminates with formation of aluminium oxide carbides and carbide.[20,75] In mixtures with graphite at $p_{CO} = 0.1$ MPa in the temperature range 2073–2173 K, condensed products are not formed. Aluminium carbide is formed above 2173 K when the partial pressure of the reduction-product aluminium in the briquet exceeds the dissociation pressure of Al_4C_3. The formation of the $Al_2O_3-Al_4C_3$ melt on metallic aluminium intensifies sharply the reduction process as a result of the appearance of liquid "bridges" between aluminium oxide and graphite, which, by dissolving carbon, promotes the preferential development of reduction reactions with participation of the liquid $Al_2O_3-Al_4C_3-Al$ melt.[28]

The absence of carbon-containing phases on the surface of the specimen[28,85] precludes an unambiguous conclusion about the reduction mechanism. These ideas can be refined by employing experimental data for the reduction to the elements of the oxides of group analogues of aluminium.

3. Reduction to Group IIIB and IIIC Elements

The oxides of Group IIIB and IIIC elements possess high thermodynamic stability[83] and are very refractory.[88] At $p_{CO} = 0.1$ MPa, the temperature of the onset of their appreciable interaction with graphite lies above 2170 K. An increase in the content of carbon without an appreciable change of the parameters of the crystal lattices of the oxides has been observed in the products formed on the surfaces of the oxides during their interaction with

graphite through space in CO.[89,90] This justified the assumption[10] that reactions involving the chemisorption of CO and its disproportionation to CO_2 and C with subsequent substitution of part of the oxide oxygen by carbon and the formation of oxide carbide and carbide phases develop on the surfaces of metal oxides. The oxide carbide and carbide phases form a solution of the type of $M_2O_3-MC_2$, which has been observed on the surfaces of scandium,[89] yttrium, lanthanum, gadolinium, and lutetium[90] oxides at 2470, 2223, 2123, 2323, and 2373 K respectively, which are lower than the melting points of the metal oxides and carbides. As a result of this, the contribution of the reactions involving reduction through the gas phase diminishes and reduction reactions with participation of the $M_2O_3-MC_2$ melt, which take place under diffusion conditions without the formation of gaseous metal-containing products, become dominant. Such change of mechanism has been reflected, in our view, by the two maxima on the kinetic curves for the reduction of bricketted mixtures (Y_2O_3 + 7C).[91]

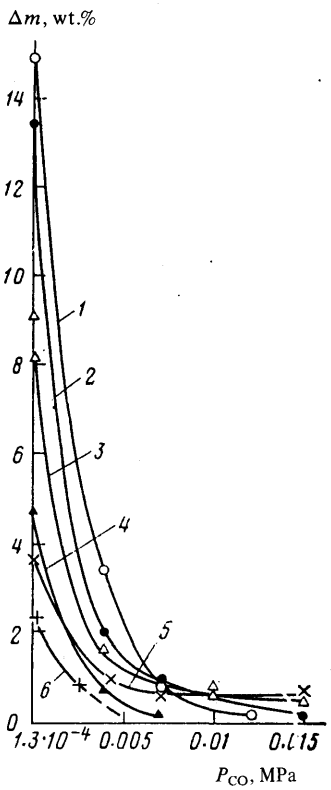


Figure 2. Decrease in the mass of metal oxides at a distance of 0.5 mm from graphite as a function of the CO pressure: 1) Al_2O_3 (2073 K); 2) La_2O_3 (1973 K); 3) Sc_2O_3 (2323 K); 4) Nd_2O_3 (1973 K); 5) Lu_2O_3 (2373 K); 6) Y_2O_3 (2223 K).[10]

At CO pressures in the space between the reactants less than 5×10^{-3} MPa, the rate of their interaction increases sharply (Fig.2). Under these conditions, the dissociation reactions of the oxides predominate with formation of the vapours of the atomic metals, their lower oxides, and atomic oxygen,[73] which react with solid carbon to give CO and the corresponding metal carbides. A similar character of the change in the degree of reduction of the oxide with decrease in pressure is observed in the reduction of aluminium,[10] which is a group analogue of the above metals.

When the reactants come into contact *in vacuo*, the interaction proceeds the gas phase up to a certain temperature with formation of the corresponding metal carbides on the carbon reductant and then, at temperatures significantly below the melting points of the metal oxides and carbides, reduction reactions with participation of the $M_2O_3-MC_2$ melt develop.

The rate of interaction of mixtures of lanthanum and gadolinium oxides with carbon *in vacuo* obeys a general correlation with the Gibbs free energy of the reduction reaction at the corresponding temperatures:[90]

$$M_2O_3+7C=2MC_2+3CO$$

This is associated with the similar chemical properties of the elements, determined by the identical numbers of valence electrons and the presence of the unfilled f^0 configuration and the stable f^7 configuration of the electrons. For the oxides of elements which are shell analogues of yttrium and lutetium, there is no similar relation in the temperature range 1900–2070 K owing to the difference between the mechanisms of the interactions with carbon which take place through the liquid and vapour–gas phases respectively. This is due to the difference between the appearance temperatures of the carbide oxide melts and the onset of the reduction through the liquid phase. Thus, when the reactants are in contact, the welding of Y_2O_3 to graphite, indicating the formation of the liquid phase, is appreciable already at 1923 K, while that of Lu_2O_3 is appreciable at 2373 K.[90]

4. Reduction to Group IVA Elements

Among the oxides of Group IVA elements, SiO_2 is the most stable and refractory. In the non-contact interaction with graphite in the presence of CO or argon or *in vacuo*, the maximum rate of reduction on the SiO_2 surface is observed at p_{CO} = 0.1 MPa.[27] A phase with a melting point close to 1823 K is then formed on the SiO_2 surface,[92] consisting of the $SiO-SiO_2$ solution.[93,94] As for the Group IIA oxides, a decrease in CO pressure[10,29] (Fig.1) promotes an increase in the rate of diffusion and mass transfer between the reactants, which compensates for the decrease in the CO concentration. At $p_{CO} < 4 \times 10^{-3}$ MPa, the contribution of reactions involving reduction by carbon monoxide diminishes and the role of SiO_2 dissociation reactions with formation of SiO and atomic oxygen,[73] which react with the carbon reductant affording CO and SiC, increases. The dominant role of the SiO_2 dissociation reactions persists in an inert gas in the presence of carbonaceous and non-carbonaceous reductants which are not in contact with the gas.[21,93]

The interaction of both liquid and solid SiO_2 with solid carbon at p_{CO} = 0.1 MPa takes place through the gas phase with participation of CO as the reductant without the formation of oxide carbide melts.[39]

The reduction of germanium, like that of its group analogue silicon, takes place through the gas phase with formation of the intermediate gaseous monoxide GeO. In the presence of solid carbon in the reducing medium, the reaction involving reduction by

carbon monoxide to gaseous GeO takes place on the GeO_2 surface, the monoxide being adsorbed on the surface of the carbon reductant and being converted into metallic germanium.[95-97]

5. Reduction to Group IVB Elements

Group IVB includes titanium and its shell analogues—zirconium and hafnium, which is the reason for the significant difference between the properties of titanium oxides and the oxides of the remaining elements in this group. In particular, it is manifested by the presence of a whole series of lower valence oxides[63] and a wider range of homogeneity of the oxide carbides than for zirconium and hafnium.[98]

The interaction of TiO_2 with CO is characterised by a very low equilibrium CO_2 pressure and has been achieved at 1373 K up to a degree of reduction of 0.08 in a circulation apparatus in which CO_2 is frozen out with liquid nitrogen.[99] On the other hand, in the presence of solid carbon,[100,101] the process proceeds vigorously. The adsorption of CO on TiO_2 surface results in the formation of Ti_3O_5 and CO_2, which react with carbon to form CO. The dissolution of CO in the defective anionic oxide sublattice and the disproportionation of CO to CO_2 and C with the subsequent substitution of part of the oxide oxygen by carbon begins after the attainment of compositions close to Ti_2O_3. The contribution of the last reaction in TiO specimens increases with increase in temperature.[100] The mass of the specimens increases and the molar ratio of the inserted elements C:O increases from 0.975 at 1773 K to 1.285 and 1.975 at 1873 and 1973 K respectively.

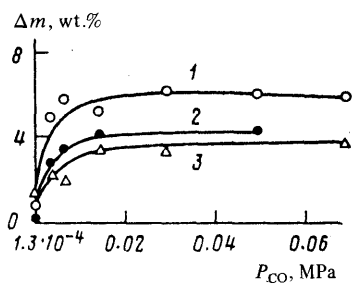


Figure 3. Decrease in the mass of metal oxides at a distance of 0.5 mm from graphite as a function of the CO pressure: 1) Nb_2O_5 (1623 K); 2) TiO_2 (1523 K); 3) Ta_2O_5 (1873 K).[10]

A decrease in the pressure of CO (Fig.3) and its replacement by an inert gas or a vacuum diminish the rate of reduction of TiO_2. In an inert gas, the dissociation of TiO_2 with formation of condensed products close in composition to $TiO_{1.9}$ predominates, whilst *in vacuo* the products have the composition $TiO_{1.87}$ [100]—the latter evaporate congruently, predominantly in the form of TiO and TiO_2,[73] and are converted into titanium carbide by reaction with solid carbon.

According to mass-spectrometric data,[12] the gas phase in the reduction of oxides of Group IVB and VB elements at $p_{Ar} = 1.33 \times 10^{-2} - 2.0 \times 10^{-3}$ MPa consists predominantly of CO and an insignificant amount of CO_2 in the range 573–1573 K. According to material balance, the overall composition of the gas phase formed is close to C_3O_2. A number of workers have therefore suggested[9,12,44,101,102] that the main reductant of titanium and other group IVB and VB elements is not CO but gaseous (or amorphous) carbon—one of the products of the decomposition of C_3O_2, whose condensate is observed on the cold parts of the furnaces. However, in the mass-spectrometric analysis of the gaseous products of the reduction to molybdenum C_3O_2 molecules have been detected experimentally at temperatures not exceeding 773 K.[103] The compound C_3O_2 is unstable and the possibility of its formation at the real reaction temperature is low.

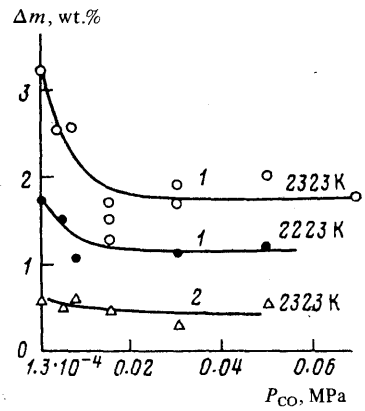


Figure 4. Decrease in the mass of metal oxides at a distance of 0.5 mm from graphite as a function of the CO pressure: 1) ZrO_2; 2) HfO_2.[10]

Zirconium and hafnium dioxides are the only thermodynamically stable solid oxides of these metals. At high temperatures (2223 to 2323 K) in the presence of carbon, they react with CO [10] to form carbides on the surfaces of the oxides. The decrease in the CO pressure to 0.01 MPa (Fig.4) influences only slightly the degree of reaction of the oxides as a consequence of diffusion-dependent obstacles arising as a result of the formation of the carbide phase. The acceleration of the interaction is observed at $p_{CO} < 0.01$ MPa in connection with the development of the dissociation reactions of the dioxides uncomplicated by the formation of any products on their surfaces and occurring via congruent evaporation from dioxides having a composition MO_{2-x} [100] predominantly in gaseous ZrO and HfO and oxygen.[73] The presence of the carbon reductant promotes a vigorous removal of the dissociation products from the surface of the oxide and the formation of ZrC, HfC, and CO on the carbon surface. At $p_{CO} = 0.1$ MPa, the amount of ZrC formed on the ZrO_2 surface increases with increase in temperature,[10] which is associated with the increase in the concentration of the active centres for

the chemisorption of CO as a result of the increase in the mobility of the crystal lattice defects in the oxides at temperatures above $0.5\,T_m$.† [62]

In vacuo, at relatively low temperatures (1523–1823 K) the reduction of particulate mixtures of the reactants also proceeds with participation of the CO adsorbed on the ZrO_2 and HfO_2 surfaces.[105-107] In the initial stage of the interaction, part of the oxygen in the anionic sublattice is removed and the oxides $ZrO_{1.98}$ and $HfO_{1.941}$ with a deficiency of oxygen are formed. In the last stage, the anionic vacancies in the lattices of the dioxides are filled with carbon, ensuring their conversion into the oxide carbide and carbide.[105,106] The formation of zirconium and hafnium oxide carbide melts is observed at 2373 and 2423 K respectively.[10]

6. Reduction to Group VB Elements

Group VB includes vanadium and its shell analogues – niobium and tantalum.[19] In contrast to the latter, vanadium forms a large number of oxides with a lower degree of oxidation and a β-phase with 15–25 at.% of oxygen.[63] In the reduction of the highest oxide to vanadium, oxides with lower degrees of oxidation are formed in succession as far as V_2O_3. In individual stages, the rate of reduction of V_2O_5 is limited by various elementary stages—in the reduction to V_2O_3 by the adsorption of CO with the subsequent diffusion of carbon and oxygen into the lattices of the oxides with formation of oxide carbide phases.[98,108]

The reduction to niobium is complicated by the formation in the condensed state of the intermediate lower oxide NbO_2 and variable-composition niobium oxide carbides.[98] For this reason, at a CO pressure above 2×10^{-3} MPa (Fig.3), the degree of conversion of Nb_2O_5 increases insignificantly owing to diffusion-dependent obstacles arising in the condensed phase.

As a result of the reduction by carbon monoxide, oxygen vacancies accumulate in the highest Group IVB and VB metal oxides and are partly filled with carbon atoms. Oxides with a lower degree of oxidation are then formed with a small amount of incorporated carbon. The CO adsorbed on the surfaces of vanadium and niobium monoxides can be absorbed, as in the case involving titanium monoxides,[100] by the defective lattices of the monoxides[102] and can also disproportionate to CO_2 and carbon atoms which fill the oxygen vacancies. This infringes the stoichiometry and causes a shift of the overall composition of the monoxide to the heterophase region of the M–O phase diagram and its decomposition with formation of an oxide with a higher degree of oxidation and the metallic phase. The metal reacts with CO and is converted into oxide carbides.[101,102,109] The absence of vanadium and niobium monoxides from the reduction products is associated with the fact, according to Shvikin,[5] that the rate of their conversion into oxide carbides having crystal lattices isostructural with those of the monoxides greatly exceeds the rates of the preceding reduction stages.

The reduction of Ta_2O_5 to tantalum is in many respects analogous to the reduction to hafnium,[10] which is due to the similarity of their properties since they are neighbours along the Period.[19] Like zirconium and hafnium dioxides, Ta_2O_5 reacts with carbon and is converted into oxide carbides with a cubic structure in accordance with the scheme described above for ZrO_2 and HfO_2, by-passing the monoxide formation stage.[98,107] The stability and composition of the oxide carbides depend on the temperature and the CO pressure in the system. An increase in the CO pressure at a specified temperature promotes not only their stability but also the expansion of the region of homogeneity, while a decrease in the CO pressure and an increase in temperature tend to increase the carbon content in the oxide carbides and bring the composition closer to that of the corresponding tantalum carbide. In the absence of contact with the solid carbon, the degree of conversion of Ta_2O_5 into the product increases with increasing CO pressure (Fig.3). However, at $p_{CO} = 2 \times 10^{-2}$ MPa, this process slows down as a consequence of the diffusion-dependent obstacles arising in the layer of products. Thus at 1873 K in the absence of contact with graphite in CO,[10] the carbide $TaC_{0.6}$ is formed on the Ta_2O_5 surface and then reacts further with the highest oxide, forming gaseous TaO and TaO_2. These oxides are adsorbed on the surface of solid carbon and are reduced to TaC. At temperatures close to 1973 K, under conditions where Ta_2O_5 is in contact with solid carbon, the interaction takes place with participation of the oxide carbide melt.[10]

7. Reduction to Group VIB Elements

Among the oxides of Group VIB elements, Cr_2O_3 is the most stable.[19,88] Its interaction with solid carbon proceeds in the initial stage with participation of CO as the reductant.[2,10,110,115] This is confirmed by the acceleration of the reduction when graphite is replaced by more active forms of carbon reductants, accelerating the gasification of carbon,[110,111] and also by the formation of reduction products on the surface of the oxide in the absence of contact with solid carbon at $p_{CO} = 0.1$ MPa.[110,112] A decrease in CO pressure in the space between the solid reactants which are not in contact with one another intensifies the reduction of Cr_2O_3 (Fig.1) [10] owing to the increase in the rate of diffusion and mass transfer which compensates for the decrease in the CO concentration. However, at $p_{CO} < 4 \times 10^{-3}$ MPa the degree of conversion of Cr_2O_3 diminishes sharply due to the decrease in the CO concentration and the oxide dissociation reactions develop preferentially, occurring at rates lower than in the reduction with carbon monoxide. The oxide Cr_2O_{3-x}, in which the concentration of oxygen corresponds to the lower limit of the region of homogeneity,[116] is formed under these conditions in the initial stage. This is followed by congruent evaporation with formation of atomic chromium and the vapours of the lower oxides CrO and CrO_2 and oxygen,[73] which react with solid carbon to give the carbide Cr_3C_2 and CO. At $p_{Ar} = 0.1$ MPa [116] and *in vacuo* ($\sim 4.6 \times 10^{-8}$ MPa), the interaction of the Cr_2O_3 specimens and solid carbon, which are not in contact, in the range 1373–2073 K [117] also includes the oxide dissociation stage.

When the solid reactants are involved in contact interaction *in vacuo* at 1773 K,[117,118] the carbide phase grows into the oxide specimen at the sites of contact between them. However, the role of this process is small owing to the extremely small area of contact in mixtures of reactants compared with their overall surface area.[2]

The interaction of Cr_2O_3 with carbon intensifies sharply at temperatures above 1773 K [116] where the reduction on the surface of chromium oxide results in the formation of the metallic Cr–C melt, which, creating a liquid contact between the reactants, ensures the preferential development of the reactions involving the reduction by the carbon dissolved in the metallic phase.

† T_m is the melting point (Ed.of Translation).

8. Reduction to Group VIIB Elements

Among the Group VIIB elements, manganese and its alloys have been obtained by the carbothermal reduction. The most stable manganese oxide is MnO, which has been detected as part of the composition of complex intermediate compounds in the reduction of concentrates and ores.[2,119,120] In a free state, without contact with solid carbon at p_{CO} = 0.1 MPa,[31] MnO reacts in the temperature range 1473–1623 K with the CO adsorbed on its surface, forming gaseous metallic manganese and CO_2. At temperatures in excess of 1623 K, the carbide Mn_7C_3 is formed on the surface of the carbon reductant. The replacement of CO by an inert gas greatly diminishes the rate of the reduction reactions on the MnO surface as a consequence of the sharp decrease in the contribution of reactions with participation of CO and the development of MnO dissociation reactions with the preferential formation of atomic manganese and molecular oxygen.[73] At temperatures close to the fusion of Mn_7C_3 (~1623 K), the contribution of the reactions of MnO with CO diminishes[31,121] owing to the formation of liquid Mn_7C_3 carbide bridges between the solid reactants and the development of reactions involving reduction by the carbon dissolved in the liquid metallic phase.

9. Reduction to Metals with Participation of Metals

Analysis of the accumulated experimental data shows that at certain temperatures reactions with participation of melts play a leading role in carbothermal reduction processes. The intensification of the reduction processes observed under these conditions is due to a number of factors; the closer contact between the fused metal oxide with the solid carbon (SiO_2 [39]); contact between the solid metal oxide and the carbon dissolved in a metallic melt (Cr_2O_3, MnO [2,31,116]); the dissolution of the initial reactants in the melt with subsequent interaction in the liquid phase (CaO,[68] Al_2O_3,[28] Group IIIB elements[89,90]), and also the stirring of the melt by the evolved gas. Under these conditions, when ionic activity is appreciable, the interaction becomes electrochemical in character. These processes have been studied in detail in the reduction of slag melts to iron, manganese, and chromium. The mechanism of the reduction of melts of this type is represented as the sum of the cathodic and anodic half-reactions, which takes place on different sections of the surface[122]

$$M^{n+1}+e=M^{(n-1)+}$$
$$M^{n+}+ne=M$$
$$C(Solid)+O^{2-}=CO+2e$$

The electron exchange necessary to maintain the electroneutrality of the phases takes place through solid carbon.

The Table presents the appearance temperatures of the melt menisci around the metal oxide specimens in their contact interaction with graphite at different CO pressures. Under these conditions and also at higher temperatures, the reduction reactions in the liquid phase assume the leading role.

10. Reduction of Complex Refractory Metal Oxides

The reduction of complex refractory oxides to the metal takes place consecutively in conformity with the thermodynamic stabilities of simple metal oxides forming part of the composition of the complex compound. Thus in the reduction of chromium ores containing chromium spinelides and chromites, the spinelides are initially reduced to iron and chromium, while at higher temperatures chromites are reduced to the metals with formation of MgO and $MgAl_2O_4$ spinel.[123] The reduction of $MgAl_2O_4$ spinel to magnesium at 2020 and 2170 K without contact with graphite at p_{CO} = 0.1 MPa takes place with participation of CO as the reductant.[124] A solid solution of Al_2O_3 in the spinel is formed as a result on the surface of the complex oxide. After the attainment of the limit of the region of its homogeneous composition, Al_2O_3 is segregated in an independent phase. The reduction reaction at the spinel–reducing gas (CO) interface take place under diffusion conditions and its rate depends on the ratio of the specific surfaces of the initial reactants.

Temperatures of the appearance of melt menisci in the contact interaction of metal oxides with graphite.[10]

Oxide	T, K	p_{CO}, MPa	Oxide	T, K	p_{CO}, MPa
Al_2O_3	2223	0.1	ZrO_2	2373	$3\cdot10^{-2}$
Sc_2O_3	2273	$1.3\cdot10^{-4}$	HfO_2	2423	0.1
Y_2O_3	2123	$1.3\cdot10^{-4}$	Nb_2O_5	1773	0.1
La_2O_3	1823	$1.3\cdot10^{-4}$	Ta_2O_5	1973	0.1
Nd_2O_3	1973	$1.3\cdot10^{-4}$	CaO	2073	$5\cdot10^{-2}$
Gd_2O_3	2073	$1.3\cdot10^{-4}$	SrO	2023	0.1
Lu_2O_3	2373	$1.3\cdot10^{-4}$	BaO	1973*	0.1
Cr_2O_3	1823	0.1	MnO	1623**	0.1
TiO_2	1923	0.1			

*According to data in Ref.30.
**According to data in Ref.31.

The interaction of the aluminosilicates with carbon also takes place in stages. In the initial stage of the reduction, gaseous SiO is formed and reacts with the carbon reductant to give silicon carbide.[125] This process is controlled by diffusion through the layer of the microporous product—α-Al_2O_3.[126] The contribution of the mullite dissociation reactions to the reduction process increases with decrease in pressure in the system. Under these conditions, the dissociation of Al_2O_3 at a lower rate than that of the formation of gaseous SiO is observed together with the thermal decomposition to gaseous SiO and solid Al_2O_3. Thus CO retains the role of the reductant in the reduction of complex oxides to the metals. When CO is diluted with an inert gas and *in vacuo*, the contribution of the reduction by carbon monoxide diminishes and the role of the metal oxide dissociation reaction increases. The reduction processes on the surfaces of solid oxides are associated with diffusion-dependent obstacles as a consequence of the segregation in an independent phase of the oxides which are more difficult to reduce to the metals.

Analysis of the accumulated experimental data shows that, in the absence of liquid phases, the interaction of solid metal oxides with carbon proceeds through the gas phase via a mechanism including reactions involving reduction by carbon monoxide and the dissociation of metal oxides. The contributions of these reactions to the overall reduction process depend on the composition of the gas phase between the reactants. At p_{CO} in excess of 4×10^{-3} MPa, the

reactions involving the reduction by carbon monoxide play a leading role, while at p_{CO} less than 4×10^{-3} MPa, the dissociation of the metal oxide predominates in an inert gas and *in vacuo*.

The character of the variation of the mass of specimens of the oxides of Group IIA elements, SiO_2, and Cr_2O_3 out of contact with graphite as a function of the CO pressure (Fig.1) indicates the presence of common features in the change of the reduction mechanism. An analogous similarity (Fig.2) has been observed for the oxides of aluminium and its group analogues (in Groups IIIB and IIIC). The formation of carbon-containing phases in chromium oxides and the oxides of Group IIIB and IIIC elements justifies the assumption that carbon monoxide is also a reductant in relation to SiO_2 and Al_2O_3. The absence of carbon-containing phases on the surfaces of oxides of Group IIA elements, Al_2O_3, and SiO_2 at p_{CO} = 0.1 MPa, interpreted by some investigators as an argument in support of the oxide-sublimation mechanism of the reduction process, is associated with the fact that, in contrast to the refractory oxides of *d* and *f* elements, the oxides of *s* and *sp* elements under the conditions of real processes are incapable of substituting part of the oxygen in the anionic sublattice by carbon atoms and of creating conditions for the appearance of carbide and oxide carbide phases.

At temperatures in excess of $0.5\,T_m$ of the metal oxides, the contribution of the reactions involving reduction by carbon monoxide on the surfaces of the solid metal oxide increases as a consequence of the increase in the concentration and mobility of the crystal lattice defects responsible for the increase in the number of centres for the chemisorption of CO.[10] The dissociation reactions become the mains ones under the conditions of a low-temperature plasma.[127]

The composition of the products of the reduction by carbon monoxide depends on the nature of the elements produced by the reduction process. The reduction of the oxides of *s* and *sp* elements and manganese with a stable $3d^5$ electron shell of the metal atom takes place via the chemisorption of CO and its subsequent oxidation by the oxide oxygen to CO_2 with formation of the vapours of the metals and the lower oxides. On the oxides of *d* and *f* elements, the chemisorbed CO disproportionates predominantly to CO_2 and carbon, which is oxidised by the oxide oxygen and also partly fills the oxygen vacancies. The kinetics of the reduction reactions on the surfaces of solid oxides of the shell analogue elements under different initial conditions obey the general correlation with the Gibbs free energy of the reduction reaction. At the corresponding temperatures, the interaction through the gas phase is limited as a consequence of the appearance of carbide oxide or carbon-saturated metallic melts.

V. OXIDATION REACTIONS OF SOLID CARBON

Reactions of two types take place on the surfaces of carbon reductants: the gasification of carbon and the formation of metal carbides in the interaction with the vapours of metals and their lower oxides. The high-temperature carbon gasification processes have been described in detail by Golovina.[128] The gasification of carbon has a multistage mechanism, which includes the chemisorption of CO_2 and the formation of intermediate complexes on active sites of the surface:

$$C + CO_2 \rightleftharpoons C(O) + CO(gas), \quad (2)$$

$$C(O) \rightleftharpoons CO(gas). \quad (3)$$

where C(O) is an intermediate complex.

At p_{CO_2} close to 0.1 MPa, the gasification reaction in the temperature range 1300–1650 K takes place not only on the surface of the carbon material but also throughout its volume. In the range 1700–2400 K, the reaction shifts to a narrow zone at the reductant surface. In this temperature range, the specific rate of the reaction is seen to diminish, passing through a minimum at 2000–2300 K as a consequence of the diffusion-dependent inhibition in the gas phase, which arises with increase in the absolute rate of oxidation of carbon. The rate of reaction depends on the number of active centres adsorbing CO_2 molecules. The decrease in the rate of reaction at 2000–2300 K, when the desorption of CO is rapid and the role of the reverse reaction (2) is small, has been attributed to the thermal deactivation of the reductant surface. At temperatures in excess of 2400 K, the depth of the reaction zone and the specific rate of the reaction again increase as a consequence of the development of the self-diffusion of carbon from the bulk phase to the reaction centre and the increase in the concentration of defects, whose number reaches a maximum at temperatures close to those corresponding to a change in the state of aggregation of the substance. This stimulates an increase in the degree of chemisorption of CO_2 and in the rate of reaction as a whole. The sublimation of graphite begins to play an appreciable role under these conditions. The disordered "amorphous" part of the reductant is then sublimed in the first place.

Carbon reductants differ significantly in their crystal structure, the type and size of pores, and the character of their distribution. The rate constants obtained for the oxidation reactions of reductants[129,130] as well as the estimation of the reactivity with respect to CO_2 [131] are valid only for specific reduction conditions. A general treatment of the results accumulated in this field established[129] that one of the main parameters determining the rate of reaction with the gas is not only the activation energy *E* but also the pre-exponential factor *A* in the Arrhenius equation, which changes on passing from one kind of material to another and obeys the relation

$$\lg A = \lg A_0 + \alpha E$$

where A_0 and α are coefficients. The relation obtained for porous (cokes, semicokes, different types of coal, anthracites) and nonporous (carbon black, carbon fibres, pyrographite) materials is universal and applicable to different textures of the material. It can be used to estimate the reactivities of reductants in relation to CO_2 in the absence of data on the size of the reaction surface. It is sufficient to know what the gas medium is and to determine the apparent activation energy for the oxidation of the reductant.

In the reduction of *s* and *sp* elements on the reductant surface, reactions with participation of the vapours of metals and the lower oxides and leading to the formation of carbides take place in addition. Therefore, if the reductant surface is blocked by the reaction products, the oxidation of carbon passes from the kinetic to diffusion conditions[90,131] with a change in the size of the specific surface.[132] Under these conditions, the growth of the layer of products, especially SiC,[132] is caused by the counterdiffusion of the metal ions and carbon along the grain boundaries and microstructural defects. The rate of diffusion of the metal ions, for example of the silicon ions in SiC, is then higher by several orders of magnitude than that of carbon ions, which promotes the preferential growth of the reaction front into the bulk of the reductant and the formation of a pseudomorphic analogue of the carbide from the carbon.

Silicon[132] is formed on the surface of the particles of the carbon reductant only after the complete conversion into silicon carbide. The partial pressure of SiO in the system should then be significantly greater than in its formation from SiO_2 and carbon.

The chemical reactivity of the reductant in relation to the metal oxide is a complex function of factors acting simultaneously (the porous structure, the specific surface, and the degree of order in the crystal structure of carbon), whose influence cannot be taken into account separately.[131] Two principal forms are present in the macrostructure of cokes—finely dispersed crystalline regions with a well developed system of pores and non-porous amorphous regions. The greater the number of crystallite intermediate forms in the microstructure and the greater their defectiveness, the larger the surface area of the reductant and correspondingly the higher its chemical reactivity.[133,134] A clear dependence of the reactivity of the reductant in relation to SiO_2 on the specific surface is observed only for petroleum cokes.[135] In other types of reductants, it depends little on the specific surface. The reactivity of different types of carbon blacks in relation to SiO_2 [135,136] depends on the degree of order in the structure. Many carbon blacks having a high specific surface are extremely compact and there is a film of high-molecular-weight products preventing the diffusion of silicide forming agents into the bulk of the particles.

In practice, the reactivity of the reductant is estimated from the intensity of its interaction with CO_2.[131] However, this method does not take into account the specific features of certain metals, whose reduction is accompanied by the formation of carbides blocking the surface of the reductant. The methods proposed for the estimation of the reactivity of the reductant from the change in the mass reacting with gaseous SiO,[137–140] with SiO_2,[131] and with CaO [141] reflect the overall result of the interaction and do not allow the determination of the influence of the surface area on the intrinsic reactivity of the reductant, which is estimated quantitatively from the ratio of the rate constants for isotypical reactions (k/k_0) carried out under identical conditions, where k_0 is the rate constant for the reaction of one of the substances in the reaction series.[142] Overall, the influence of the surface of the reductant and of its reactivity on its chemical activity in relation to the metal oxide being reduced (for example, SiO_2) has been estimated[39] from the quantity

$$A = S k$$

where S is the initial surface of the reductant ($m^2\ kg^{-1}$) and k the rate constant for the reaction of carbon ($kg\ m^{-2}\ s^{-1}$).

Thus the chemical activity of the reductant depends on two factors acting simultaneously, its specific surface and its reactivity. The activity of the reductant can therefore be increased not only by selecting the necessary degree of dispersion and hence the specific surface of the reductant[139,143,144] but also by increasing its reactivity. The latter is achieved by introducing mineral admixtures,[131,133,135,145] by mechanochemical treatment together with the metal oxides to be reduced,[12,146] and by γ-irradiation,[147] which ensures the appearance of oxide–carbon–oxygen complexes at additional defects in the carbon structure.

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It follows from the analysis of the data described that the observed difference in the interaction of refractory metal oxides with carbon are correlated with the differences in the fundamental properties of the metal atoms generated in the reduction process, which are reflected in the Periodic System of the elements. This made it possible to deduce a general basis for the description of the interactions of solid metal oxides with carbon, according to which they proceed via an adsorption-dissociative mechanism including reactions involving reduction by carbon monoxide in combination with reactions involving the gasification of solid carbon by its dioxide and the dissociation of the metal oxide. At CO pressures in the space between the reactants in excess of 4×10^{-3} MPa, the reactions involving reduction by carbon monoxide develop preferentially. The contribution of the metal oxide dissociation reactions to the overall reduction process is insignificant under these conditions. On decrease in the CO pressure to less than 4×10^{-3} MPa, *in vacuo*, and in an inert gas, the metal oxide dissociation reactions make the main contribution to the reduction process.

The differences in the interaction of certain metal oxides with carbon at p_{CO} close to 0.1 MPa depend on the properties of the oxides, which are determined by the electronic structure of the reduction product metal atoms. Thus the reduction of the oxides of *d* and *f* elements by carbon monoxide in the presence of solid carbon is accompanied by the liberation of CO_2 to the gas phase, while the reduction of the oxides of *s* and *sp* elements results in addition in the evolution of the vapours of the metals and their lower oxides, which block the surfaces of the carbon reductants by the corresponding carbides. The CO adsorbed on the surfaces of the oxides of *s* and *sp* elements is oxidised by the oxygen of the oxides to CO_2, while on the surfaces of the oxides of *d* and *f* elements it disproportionates to CO_2 and carbon, which is oxidised by the oxide oxygen and partly fills the oxygen vacancies, forming solutions of carbon in the oxides and carbon-containing phases. The existence of groups of oxides for which there are general correlations between the rate of reduction and the Gibbs free energy of the reduction reaction has been established in relation to the oxides of elements, which are shell analogues of calcium, strontium, and barium, and also lanthanum and gadolinium oxides.

The chemical activity of the reductant depends on the two factors acting simultaneously: its specific surface and its reactivity. The latter can be increased by introducing mineral admixtures, by mechanochemical treatment, and by γ-irradiation.

It is noteworthy that many ideas about the interaction of CO with the surfaces of solid metal oxides require confirmation by refined experimental methods. It is essential to accumulate qualitatively new information about the elementary steps in the reduction process by employing research methods from adjacent fields of science. Overall, the views formulated on the mechanism of the reduction process make it possible to estimate the interrelation between the individual stages of the processes, to select the optimum compositions of the gas phase, the carbon reductants, etc., and to influence the intensity of technological processes.

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Photon Transfer Reactions in Free Radicals. Spin pH Probes

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The kinetics and thermodynamics of proton transfer processes with participation of short-lived and stable radicals are surveyed. The extensive possibilities for the use of pH-sensitive nitroxy-radicals for the measurement of acidity in microheterogeneous chemical and biological systems, including cells, are demonstrated.
The bibliography includes 102 references.

CONTENTS

I. Introduction 824
II. Theoretical examination of proton transfer reactions in radicals 825
III. Proton exchange in short-lived radicals 825
IV. Proton exchange in stable nitroxy-radicals 826
V. The use of nitroxy-radicals as pH probes 835

I. INTRODUCTION

Proton transfer is one of the commonest reactions in organic chemistry.[1,2] The study of the proton transfer reaction is timely because of its important role in acid and alkaline catalysis[2,3] and in technological and biological processes.[4] The simplicity of these reactions, which proceed without the interaction of the electron shells of the reactants, making it possible to model the given reactions by methods of theoretical chemistry and promoting a deeper understanding of the nature and kinetics of the elementary step in condensed media, has also attracted physical chemists.[1,2,5] The large hydrogen isotope effect has stimulated numerous investigations of such effects in proton transfer reactions. They serve as an important test of the theory of isotope effects and yield significant information about the mechanisms of the processes considered.[5,6] As a consequence of the unique properties of the proton (the absence of an electron shell, anomalous mobility), proton transfer reactions are the fastest reactions occurring in solution; this gives rise to methodological complexities in the study of the kinetic parameters of such reactions. Relaxation methods (methods based on the abrupt change in temperature, pressure, the electric field pulse, etc.) as well as the NMR method (the study of the broadening of the ^{1}H and ^{17}O lines in the NMR spectra) are most often used to study the kinetics of proton transfer.[1] The relaxation methods are based on the observation of the kinetics of the return of the system to the equilibrium position (by optical or electrical procedures) after a rapid change in external parameters; their application is restricted to reversible proton transfer reactions. The NMR method is free from this limitation, since its application is based on the analysis of the form of the spectrum of the molecule participating in the reaction. However, when it is used, it is essential to have large concentrations of the reactants and, in the case of complex unresolved NMR spectra, the problem of the interpretation of the experimental data arises. Methods which make it possible to follow directly the state of the reacting species in the course of the proton exchange process (among the procedures indicated, the NMR method is of this kind) are of greatest interest. Evidently, the development of new methodological approaches which yield quantitative information about the kinetic and thermodynamic characteristics of proton exchange is a problem of extremely urgent current interest. The use of the EPR method, which is highly sensitive and makes it possible to observe directly the paramagnetic reactant and to obtain quantitative information about the kinetics of proton transfer, is promising. It may be expected that the application of the EPR method to proton transfer reactions in stable radicals will make it possible to employ such reactions as model processes for securing quantitative information about the influence of the steric factor, the solvent, and the electron-donating and electron-accepting substituents on the kinetics and equilibrium parameters of proton transfer. When a reversible proton transfer reaction takes place in radicals, the pH may influence the EPR spectra of the radicals. The possibility of measuring pH by the EPR method thus arises.

The measurement of pH is one of the most important problems in chemistry and biology, since the occurrence of an enormous number of chemical reactions and many processes involved in the vital activity of cells and cell organelles depends on this quantity. The electrometric method using glass electrodes is traditionally employed for this purpose.[7] Its main disadvantage is the large size of the glass electrodes and the impossibility of introducing them into closed structures (cell organelles, model membrane vesicles, etc.). Despite the recent development of microelectrode pH measurements,[8] this limitation in most cases precludes the use of glass electrodes for the measurement of local changes in pH (within the structures indicated, at interfaces, etc.). Fluorescent probes and the NMR method are therefore widely used nowadays in biological systems on the basis of the influence of the pH of the medium on specific characteristics of the spectra of these probles (fluorescence intensity, the chemical shift).[9-16] The application of fluorescent probes is restricted by the complexities in the interpretation of the fluoresecence intensity, which is sensitive to the interaction of the probe with the lipid membrane, to the type of buffer employed, to the ionic strength of the solution, etc. A significant limitation of the NMR method is its low sensitivity. The employment of stable nitroxy-radicals (NR) as pH probes is therefore promising, in view of the high sensitivity of the EPR method and the major advances in the organic chemistry of NR.[17,18] The considerable influence of pH on the EPR spectra of stable NR observed recently[19-21] makes it possible to take a fresh look at the prospects for their employment in the study of the mechanisms of proton transfer reactions and as pH probes.

The present review examines the results of studies of the influence of pH on the EPR spectra of short-lived and stable radicals of different types. The proton transfer in imidazoline and

imidazolidine radicals has been considered in especially great detail, because these radicals actually make it possible to obtain information about the mechanism of the proton transfer and are most promising for use as pH probes in various systems, including biological systems.[22]

II. THEORETICAL EXAMINATION OF PROTON TRANSFER REACTIONS IN RADICALS

The reversible proton transfer reaction (proton exchange) between the conjugate base (the $\dot{R}$ radical) and acid (BH^+) is described by the equation

$$\dot{R} + BH^+ \underset{k_r}{\overset{k_f}{\rightleftarrows}} \dot{R}H^+ + B \ . \qquad (1)$$

A necessary condition for the application of the EPR method in following the course of reaction (1) is a difference between the magnetic-resonance parameters of the radical in the $\dot{R}$ and $\dot{R}H^+$ forms. In this case, reaction (1) should lead to rapid exchange between the corresponding components of the EPR spectra of the radicals in the $\dot{R}$ and $\dot{R}H^+$ forms. The line shape of the EPR signal $G(X)$ in the case of rapid exchange involving two positions, corresponding to the $\dot{R}$ and $\dot{R}H^+$ forms of the radical, is described by the equation[23]

$$G(X) = I_m \left\{ iG_0 \frac{\tau_{RH^+} + \tau_R + \tau_{RH^+}\tau_R (p_{RH^+}\alpha_R + p_R\alpha_{RH^+})}{(1 + \alpha_R\tau_R)(1 + \alpha_{RH^+}\tau_{RH^+}) - 1} \right\} \ , \qquad (2)$$

where G_0 is a constant coefficient, τ_R and τ_{RH^+} are the lifetimes of the radical in the $\dot{R}$ and $\dot{R}H^+$ forms respectively, $p_R = \tau_R/(\tau_R + \tau_{RH^+})$, $p_{RH^+} = \tau_{RH^+}/(\tau_R + \tau_{RH^+})$, $\alpha_R = (1/T_2)_R - i\gamma X$, $\alpha_{RH^+} = (1/T_2)_{RH^+} - i\gamma(X + \Delta\omega/\gamma)$, $\Delta\omega$ is the difference between the frequencies of the corresponding lines in the EPR spectra of the radical in the $\dot{R}$ and $\dot{R}H^+$ forms, $(T_2)_R$ and $(T_2)_{RH^+}$ are the transverse relaxation times of the radicals $\dot{R}$ and $\dot{R}H^+$ respectively, and γ is the gyromagnetic ratio of the electron. The variable X is linked to the "permanent" magnetic field H_0 by the relation $X = H_0 - H_0^R$, where H_0^R is the field strength corresponding to the centre of the EPR signal of the radical in the form $\dot{R}$.

In conformity with Eqn.(2), different cases of exchange are realised experimentally: rapid ($1/\tau_R$, $1/\tau_{RH^+} \gg \Delta\omega$), slow ($1/\tau_R$, $1/\tau_{RH^+} \ll \Delta\omega$), or intermediate ($1/\tau_R$, $1/\tau_{RH^+} \simeq \Delta\omega$) in terms of the EPR time scale. Regardless of the frequency of the $\dot{R} \rightleftarrows \dot{R}H^+$ exchange, the ratio τ_R/τ_{RH^+} can be determined from the EPR spectra using Eqn.(2). On the other hand, analysis of Eqn.(2) shows that the determination of the lifetimes τ_R and τ_{RH^+} is possible only in the case of the intermediate exchange.[23] In the presence of well resolved lines in the EPR spectra, Eqn.(2) simplifies greatly and it is sufficient to know the positions and widths of the lines in order to find τ_R and τ_{RH^+}.[23] Knowing the ratio τ_R/τ_{RH^+}, it is possible to determine the equilibrium constant K:

$$K = k_r/k_f = \frac{[BH^+][\dot{R}]}{[B][\dot{R}H^+]} = \frac{\tau_R}{\tau_{RH^+}} \frac{[BH^+]}{[B]} \ . \qquad (3)$$

When reaction (1) describes the exchange with a solvent proton ($BH^+ \equiv H^+_{solv}$, i.e. a solvated proton), Eqn.(3) relates the equilibrium constant K to the concentration of protons $[H^+]$, i.e.

$$\left(K = \frac{\tau_R}{\tau_{RH^+}} [H^+]\right),$$

which leads to the possibility, in principle, of using radicals as pH probes.

The quantities τ_R and τ_{RH^+} determine the kinetic parameters of reaction (1), namely the rate constants k_f and k_r:

$$k_f = \frac{1}{\tau_R}[BH^+], \quad k_r = \frac{1}{\tau_{RH^+}}[B] \ . \qquad (4)$$

Thus in the cases indicated analysis of the form of the EPR signal makes it possible to obtain quantitative information about the thermodynamics and kinetics of the proton exchange in radicals.

In the case of irreversible proton transfer reactions in radicals, the difference between the magnetic-resonance parameters of the $\dot{R}$ and $\dot{R}H^+$ forms permits the direct recording by the EPR method of the accumulation (disappearance) of one of the forms of the radical. The characteristic times accessible to investigation by the EPR method are limited by the time required to "start" the reactions (for example, in the stopped flow method, the time taken to mix the reactants is $\gtrsim 10^{-3}$ s).

III. PROTON EXCHANGE IN SHORT-LIVED RADICALS

Changes in the EPR spectra of a series of alcohol radicals $\dot{R}OH$ in an acid medium have been observed.[24–26] These changes are manifested by the reversible merging of the lines of the doublet, which arises from the hyperfine interaction (HFI) with the hydroxyl proton, to a singlet as a consequence of the proton exchange:

$$\dot{R}OH + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \dot{R}OH_2^+ \ . \qquad (5)$$

Reaction (5) alters the projection of the nuclear spin of the hydroxyl proton of the ROH radical and thus leads to frequency exchange between the lines of the doublet due to the HFI with the given proton. Analysis of the positions and widths of the lines in the EPR spectra of the $\dot{R}OH$ radicals made it possible to determine the proton exchange rate constant k_1, which is in the range 6.5×10^6 to 1.8×10^8 litre mol^{-1} s^{-1}. The temperature variation of the rate constant for the protonation of the hydroxymethyl radical k_1, characterised by the activation energy $\Delta E = 2.8$ kcal mol^{-1}, has also been found.[26]

Whereas the influence of pH on the EPR spectra is a consequence of the protonation of the OH group in hydroxyalkyl radicals in an acid medium in the studies[24–26] mentioned above, in other investigations[27–29] such influence was caused by the deprotonation of the OH group in accordance with the reaction

$$\dot{R}OH + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \dot{R}O^- + H_2O \ . \qquad (6)$$

The difference between the EPR spectra of the $\dot{R}OH$ and $\dot{R}O^-$ forms made it possible to determine the pK of the radicals investigated and, in the two cases where intermediate exchange was observed, also the rate constants: pK = 11.51 and $k_1 = 7 \times 10^9$ litre mol^{-1} s^{-1} for the radical $CH_3\dot{C}HOH$ and pK = 1203 and $k_1 = 9 \times 10^9$ litre mol^{-1} s^{-1} for the radical $(CH_3)_2\dot{C}HOH$.[27–29] It is noteworthy that, in the case of slow and intermediate exchange, the EPR spectra of the test radicals[28] had a very complex form at pH $\simeq$ pK. Therefore 1 M orthophosphoric acid with pK = 12.32 was added to the solution of the radical. The rate of proton exchange then increases,[30,31] which simplifies the EPR spectrum. The essential feature of the proposed approach can be readily understood by considering all the proton exchange reactions with participation of the radical and the added buffer B:[30]

$$\begin{aligned} &\text{(a)}\ \dot{R} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \dot{R}H^+ \ , \\ &\text{(b)}\ B + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} BH^+ \ , \\ &\text{(c)}\ \dot{R} + BH^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \dot{R}H^+ + B \ . \end{aligned} \qquad (7)$$

The quantities pK_1, pK_2, and pK_3 are linked by the relation[31]

$$pK_3 = pK_1 - pK_2 . \quad (8)$$

The addition of a buffer to the system alters only the kinetic parameters of the $\dot{R} \rightleftarrows \dot{R}H^+$ exchange (τ_R, τ_{RH^+}), while the equilibrium in this reaction (τ_R/τ_{RH^+}) is undisturbed:

$$\begin{aligned} &(a)\ 1/\tau_R = k_3[BH^+] = k_3B_0/(1 + 10^{pH-pK_3}) , \\ &(b)\ 1/\tau_{RH^+} = k_{-3}[B] = k_{-3}B_0/(1 + 10^{pK_3-pH}) , \\ &(c)\ \tau_{RH^+}/\tau_R = [RH^+]/[R] = 10^{pK_1-pH} , \end{aligned} \quad (9)$$

where $B_0 = [B] + [BH^+]$ is the buffer concentration; here it is understood that $k_3[BH^+] \gg k_1[H^+]$, and $k_{-3}[B] \gg k_{-1}$. According to Eqns.(9), the most effective acceleration of the exchange (decrease in τ_{RH^+} and τ_R) is observed under conditions where $pK_1 \simeq pK_2$.

The proton exchange reaction between two forms of the glycine radical has been investigated:

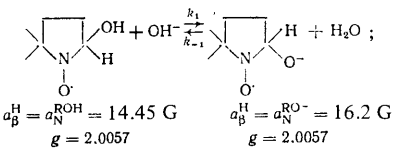
$$NH_2{-}\dot{C}H{-}COO^- + H_2PO_4^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} NH_2{-}\dot{C}H{-}COOH + HPO_4^{2-} . \quad (10)$$

In the absence of a buffer, the proton exchange via reaction (7a) leads to slow exchange between the corresponding lines of the EPR spectrum of the glycine radical. The addition of the phosphate buffer ($pK_2 = 6.4$) made it possible to pass to the region of the intermediate exchange and to calculate the rate constants for the proton exchange reaction (10): $k_3 = (2.5 \pm 0.5) \times 10^9$ litre mole^{-1} s^{-1} and $k_{-3} = (1.4 \pm 0.5) \times 10^9$ litre mol^{-1} s^{-1}. Rapid $\dot{R} \rightleftarrows \dot{R}H^+$ exchange occurs in 0.5 M phosphate buffer and $pK_1 = 6.65$ for the carboxy-group in the glycine radical was calculated from the pH dependence of the HFI constants: a_H^{CH}(pH) and a_N(pH). In the analysis of the a(pH) dependences use was made of Eqn.(11), which can be readily obtained for the case of rapid exchange from Eqns.(2) and (9c):

$$a(pH) = a_R \cdot p_R + a_{RH^+} \cdot p_{RH^+} = (a_R + a_{RH^+} \cdot 10^{pK_1-pH})/(1 + 10^{pK_1-pH}) , \quad (11)$$

where a_R and a_{RH^+} are the HFI constants of the radicals in the $\dot{R}$ and $\dot{R}H^+$ forms respectively.

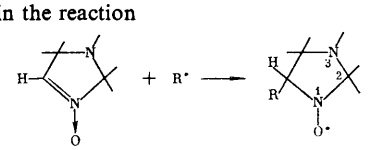
An interesting case of the manifestation of the deprotonation of the OH group has been observed[32] in a hydroxynitroxy-radical:



(12)

The protonated ($\dot{R}OH$) and deprotonated ($\dot{R}O^-$) forms of the radical differed in their HFI constants. In the region where pH $\simeq$ pK, the rapid $\dot{R}OH \rightleftarrows \dot{R}O^-$ exchange was observed and the $a_N = a_\beta^H$(pH) dependence was described by Eqn.(11).

The influence of pH on the EPR spectra of a series of spin adducts formed in the reaction



(13)

R=OH, O_2^-(HO$_2$), CH_2OH, O_4^- .

has been observed.[33] The change in the EPR spectra of the short-lived NR formed via reaction (13) in the pH range 2–5 was explained by the authors of the above study by the protonation of the N(3) atom. A number of studies[34–38] have been devoted to the investigation by the EPR method of the proton exchange reactions in semiquinone, semidione, and other short-lived radicals.

Thus the manifestations of the proton exchange in the EPR spectra of short-lived radicals have been fairly thoroughly investigated. Analysis of these spectra makes it possible to measure both the equilibrium constants of the proton exchange reactions and the bimolecular protonation constants. It has been noted in a number of studies that the pK of the radicals are appreciably lower than those of the corresponding diamagnetic molecules,[27–31] which has been attributed to the electron-accepting influence of the radical centre. The protonation constants are in the range $5 \times 10^6 - 10^{10}$ litre mol^{-1} s^{-1}.[24–26,28,30,31,35–37]

The use of the radicals considered as pH probes is in general impossible as a consequence of their instability.

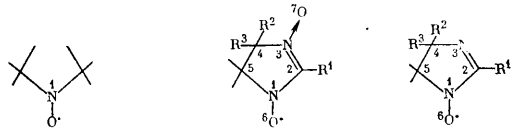
IV. PROTON EXCHANGE IN STABLE NITROXY-RADICALS

As can be seen from the previous Section, the presence of groups capable of being protonated (deprotonated) in the structure of the radical in the immediate vicinity of the radical centre leads to a difference between the EPR spectra of the protonated ($\dot{R}H^+$) and deprotonated ($\dot{R}$) forms of the radical. However, the simultaneous fulfillment of two requirements—the presence of a functional group near the radical centre and the stability of the radical—is not easy. The manifestation of proton exchange in the EPR spectra of stable radicals has therefore been recorded only in rare instances.

The greatest changes in the parameters of the EPR spectra of NR are to be expected when the latter are protonated at a radical centre where the main bulk of the spin density is localised.

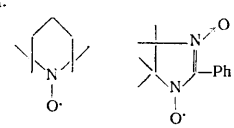
1. Protonation of Nitroxy-radicals at the Radical Centre

The spin density in di-t-alkylnitroxy-radicals is localised mainly on the nitroxy-fragmnent [$\rho_O^\pi \simeq 0.6$; $\rho_{N(1)}^\pi \simeq 0.4$ [39]], in nitronylnitroxy-radicals (NNR) it is localised on the two nitroxy-groups [$\rho_{N(1)}^\pi \simeq \rho_{N(3)}^\pi \simeq 0.22$; $\rho_{O(6)}^\pi \simeq \rho_{O(7)}^\pi \simeq 0.21$ [39]], while in iminonitroxy-radicals (INR) it is localised on the nitroxy-fragment and nitrogen of the imino-group [$\rho_{N(1)}^\pi \simeq 0.38$; $\rho_{O(6)}^\pi \simeq 0.4$; $\rho_{N(3)}^\pi \simeq 0.16$ [40]]:



di-t-alkyl nitroxide nitronyl nitroxide iminonitroxide

The N–O fragment in NR is protonated only in acid media.[41–43] Such protonation of the radical (I) in aqueous 80% sulphuric acid solution increases the constant $a_N(\Delta a_N = 5.7$ G) and decreases the g-factor ($\Delta g = 0.0013$) of the radical and also leads to the appearance of additional doublet splitting ($a_H = 3.12$ G) due to the HFI with the added proton:[43]



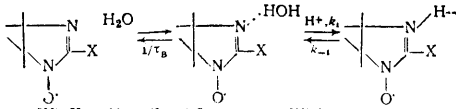
(I) (II)

$a_N = 15.87$G $a_{N(1)} = 7.5$G

$g = 2.0059$ $a_{N(3)} = 7.5$G

For the majority of NR, protonation at the oxygen atom of the N—O fragment cannot be observed, since in aqueous solutions this process is accompanied by the disproportionation of the NR to the corresponding oxoammonium and hydroxyammonium cations.[44] The protonation of the oxygen atom in the same fragment of NNR in aqueous solutions has not been observed as a consequence of the disproportionation of these radicals in an acid medium.[45] However, in benzene, in the presence of trifluoroacetic acid, it has been possible to observe the EPR spectrum of the radical (II) protonated at the oxygen atom of the nitroxy-group; the constants of the HFI with both nitrogen atoms then decreased (Δa_N = 1.8 G; $\Delta a'_N$ = 2.8 G) and an additional doublet splitting appeared due to the HFI with the added proton (a_H = 4.7 G).[45]

In contrast to the di-t-alkylnitroxy-radicals[41–43] and the nitronyl-nitroxy-radicals,[45] protonated at the nitrogen atom of the imino-group N(3), which is more basic than the nitroxy-group, has been observed for INR:[40,46]



(14)

(III) X = Ph; pK = 1.9; $a_{N(1)}$ = 9.9G; $a_{N(3)}$ = 4.5G
(IV) X = NH_2; pK = 6.4;
(V) X = N $(CH_3)_2$; pK = 6.8
(III)·H^+ $a_{N(1)}$ = 6.2G; $a_{N(3)}$ = 4.9G; a_H = 4.6 G

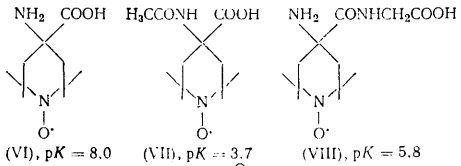
The large spin density in INR at the N(3) atom is responsible for the greater changes in the constants of the HFI with the nitrogen atom when the latter is protonated [Eqn.(14)]. The constant for the HFI with the added proton a_H in the protonated form of the radical (III) at pH > 1 is not observed as a consequence of the rapid (in terms of the EPR time scale) exchange [via reaction (14)]. The determination of the H^+ concentration at which additional doublet splitting due to the HFI with the added proton appears in the EPR spectrum of the radical form (III)-H^+ made it possible to estimate the lifetime of the $=N\cdots HOH$ hydrogen bond in the radical (III): $\tau_H \simeq 2 \times 10^{-10}$ s.[46] The condition for the rapid $\dot{R} \rightleftarrows \dot{R}H^+$ exchange in the radical (III) makes it possible to determine the lower limit to the bimolecular protonation constant: $k_1 \gg 5 \times 10^7$ litre mol^{-1} s^{-1}. According to other data,[40] the averaging of the signals of the $\dot{R}$ and $\dot{R}H^+$ forms of the radical (III) is incomplete and the exchange has a measureable effect on the position and width of the lines of the EPR signal; this made it possible to calculate the rate constant for the protonation of the radical (III): $k_1 \simeq 10^9$ litre mol^{-1} s^{-1}. The values of k_1 have also been obtained for three other INR and were found to lie in the range $3 \times 10^6 - 10^9$ litre mol^{-1} s^{-1}.[40]

Iminonitroxy-radicals can also form equilibrium complexes in aqueous solutions not only with the proton but also with a series of diamagnetic metals [Hg(II), Zn(II), Cd(II); Ag(I), etc.[40,47]]. Complex formation with participation of the N(3) atom in the INR and of the metal leads to a change in the HFI constants $a_{N(1)}$ and $a_{N(3)}$, which can be recorded by EPR, and to the appearance of HFI with the nucleus of the metal [the HFI constant $a_{Hg} \simeq 40$ G for Hg(II) [40]].

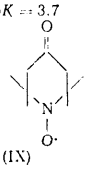
Among the radicals investigated in a series of studies,[40–43,45,46] only two [(IV) and (V)] can be used as pH probes in aqueous solutions in the pH range of practical interest. However, the interpretation of the EPR spectra of the radicals (IV) and (V) at pH $\simeq$ pK is extremely complex, since these spectra are formed as a result of the superposition of the signals of the $\dot{R}$ and $\dot{R}H^+$ forms, in each of which HFI with three non-equivalent nitrogen atoms and protons of the substituent X is manifested.[40]

2. Protonation of the Functional Groups of Nitroxy-radicals

The influence of pH on the EPR spectra of radicals of the piperidine type [(VI)—(VIII)] containing functional groups capable of being protonated (deprotonated) at C(4) has been observed:[48]

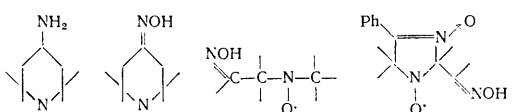


(VI), pK = 8.0 (VII), pK = 3.7 (VIII), pK = 5.8

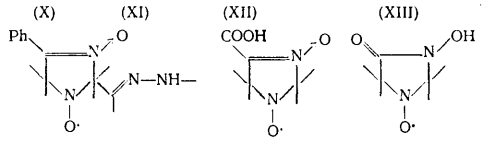


(IX)

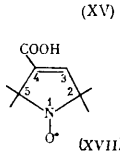
A decrease in the HFI constant a_N(Δa_N = 0.15—0.3 G) and an increase in the g-factor ($\Delta g \simeq 0.0001$) have been observed for these radicals with decrease in pH. On the other hand, the EPR spectrum of the radical (IX), which has no group capable of protonation at C(4), did not change over the pH range 2—12. The authors[48] therefore explained the observed changes in the EPR spectra by the reversible protonation of the amino-group in the radicals (VI) and (VIII) and the deprotonation of the carboxy-group in the radical (VII). The slow exchange between the $\dot{R}$ and $\dot{R}H^+$ forms of the radicals (VI)—(VIII) leads to the asymmetry of the EPR spectra, which is manifested most markedly by the decreased intensity of the high-field component. It has been suggested that the pH dependence of the consant a_N and also of the parameters characterising the asymmetry of the signal (the ratio of the intensities of the central high-field components, etc.) be used to determine the pK of the radical by the EPR method. The pH dependence of a_N can be employed to determine the pK also in the absence of the asymmetry of the signal, as in the case of the rapid $\dot{R} \rightleftarrows \dot{R}H^+$ exchange. The sensitivity of the EPR spectrum of the radical (X) of the piperidine type, with the NH_2 group at C(4), to the pH has been reported.[49] However, the authors[49] did not interpret the observed slight increase in the HFI constant ($\Delta a_N \simeq 0.13$ G) in the alkaline pH range 8 to 10.5, which in our view is due to the deprotonation of the NH_2 group (pK = 9.5 [50]):



(X) (XI) (XII) (XIII)



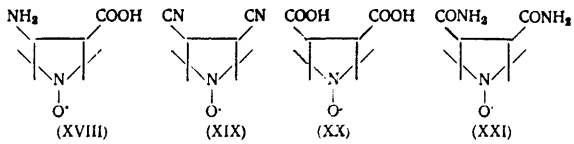
(XIV) (XV) (XVI)



(XVII)

For another radical of the piperidine type with the =NOH group at C(4) [the radical (XI)], an increase in a_N in an alkaline medium has also been observed (Δa_N = 0.16 G).[51] The observed reversible

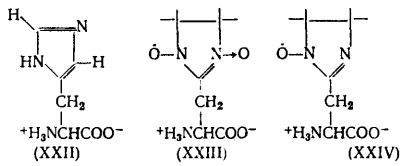
change in a_N over the pH range 10–12.8 was explained by the reversible deprotonation of the =NOH group. This is confirmed by the similar pK values found by the EPR method from the dependence of a_N on pH for three radicals of different types containing the =NOH group:[51] the piperidine type radical (XI) (pK = 11.35; Δa_N = 0.16 G), the acyclic di-t-alkylnitroxy-radical (XII) (pK = 11.55; Δa_N = 0.34 G), and the radical (XIII), which is of the 3-imidazoline 3-oxide type (pK = 10.7; Δa_N = 0.22 G). Much lower pK values have been found for the 3-imidazoline 3-oxide type radicals (XIV) and (XV) with other functional groups, amounting to 1.6 and 1.9 for the =N–NH group in the radical (XIV) (Δa_N = 0.47 G) and the COOH group in the radical (XV) (Δa_N = 0.15 G) respectively. A difference between the EPR spectra of the $\dot{R}$ and $\dot{R}H^+$ forms of the imidazolidine type radicals (XVI), which are analogues of hydroxamic acid (pK = 7.0; Δa_N = 0.24 G), and the pyrrolidine type radicals (XVII) with the carboxy-group at C(4) (pK = 3.5; Δa_N = 0.31 G) [51] has also been observed. The influence of pH on the EPR spectra of the pyrrolidine type radicals (XVIII)–(XXI) has been reported recently:[52]



(XVIII) (XIX) (XX) (XXI)

The spectra of these radicals at pH 2 and pH 12 differed in the values of the HFI constant (Δa_N = 0.3–0.5 G). However, in contrast to Nakie et al.[48] and Khramtsov et al.,[51] Matthew and Dodd[52] presented no data concerning the pH dependence of the parameters of the EPR spectra (a_N, g-factor), so that the question of the pK of the groups protonated in the radicals (XVIII)–(XXI) remains open. The prospects for the use of these radicals as pH probes are also obscure. We may likewise note that the difference between the EPR spectra of the $\dot{R}$ and $\dot{R}H^+$ forms can be determined by the influence of the protonation of the functional groups of the radical on its intermolecular or intramolecular interactions.

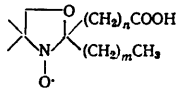
Changes in the EPR spectra of a series of radical analogues of histidine (XXII) have been observed as a function of pH:[53]



(XXII) (XXIII) (XXIV)

The protonation of the carboxy-group in the radicals (XXIII) and (XXIV) altered the constants for HFI with the non-equivalent β-protons of the methylene group. This was explained by the ion–dipole interaction between the electron-deficient nitronylnitroxy-ring [for the radical (XXIII)] or the iminonitroxy-ring [for the radical (XXIV)] and the carboxylate anion. The protonation of the carboxy-group disturbs such interaction and shifts the equilibrium between the conformations responsible for the non-equivalence of the constants for the HFI with the methylene protons. An analogous ion–dipole interaction between the imidazole ring and the carboxylate ion in histidine has been observed by NMR.[53]

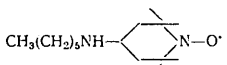
The pH influences the EPR spectra of the spin-labelled aliphatic acids (XXV) and (XXVI) in an aqueous lecithin suspension:[54]



(XXV) $m = 12$, $n = 3$
(XXVI) $m = 5$, $n = 10$

The spectra of the radicals (XXV) and (XXVI) have the form characteristic of immobilised radicals and the order parameter S, characterising the degree of hindrance of the rotation of the NR,[55] depended on the pH of the medium in the pH range 4–7. Since no influence of the pH on the EPR spectra of the methyl ester of the radical (XXVI) was observed under these conditions, the pH-dependent changes in the spectra of the radicals (XXV) and (XXVI) were explained[54] by the deprotonation of the carboxy-group. Since the carboxy-group is very remote from the N–O· radical fragment in the radicals (XXV) and (XXVI) [in the radical (XXVI) they are separated by a chain of 10 CH_2 groups], the observed differences between the EPR spectra of the protonated and deprotonated forms of the radicals are apparently entirely due to the interaction of both forms with the lipid phase, which leads to a difference between their rotational characteristics manifested in the EPR spectra.

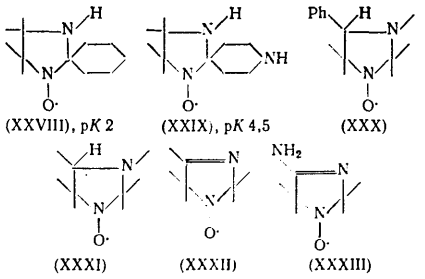
The influence of pH on the EPR spectrum of the NR (XXVII) in an aqueous suspension of lipid vesicles (liposomes) has been investigated:[56]



(XXVII)

In this medium, the radical (XXVII) is distributed between the aqueous and lipid phases, the EPR signal in the lipid phase being greatly broadened as a consequence of immobilisation. The partition coefficient of the radical (XXVII) between the aqueous and lipid phases varies by a factor of ~10 in the pH range 3.5–11.5, which has been explained by the difference between the partition coefficients of the form of the radical (XXVII) protonated at the third nitrogen atom linked to the C(4) atom and of its non-protonated form. The radicals (XXV) and (XXVII) have been used[57,58] to investigate the transmembrane proton transport through a model phospholipid membrane. The different permeabilities of the membranes to the $\dot{R}$ and $\dot{R}H^+$ forms of the radical (X) have been used to determined ΔpH on natural membranes.[50,59,60] Since the sensitivity of the EPR spectra of the radicals (XXV)–(XXVII) to pH is observed only when the solution contains the lipid phase, their use for the direct measurement of pH in general is not possible.

In 1982, the influence of pH on the EPR spectra of NR of the imidazoline and imidazolidine types was observed independently in a number of studies.[19–21] Rapid proton exchange between the $\dot{R}$ and $\dot{R}H^+$ forms of the radicals (XXVIII) and (XXIX), differing in the HFI constants ($\Delta a_N \simeq$ 1.2 G) was noted by Keana et al.[19] Khramtsov et al.[21] observed different cases of proton exchange (rapid or slow) for the radicals (XXX)–(XXXIII), whose $\dot{R}$ and $\dot{R}H^+$ forms differed both as regards the HFI constants (Δa_N = 0.8–1.2 G) and the g-factors (Δg = 0.0002–0.0003). As a consequence of such appreciable differences, the radicals of the imidazoline and imidazolidine types are most promising for the study of the mechanisms of the proton exchange reactions by EPR and also for use as pH probes:



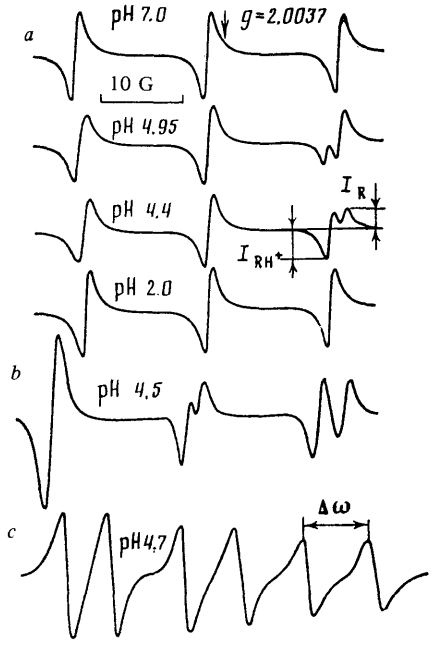
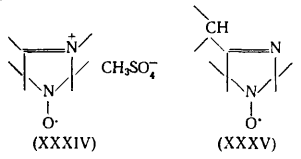


Figure 1. EPR spectra of an aqueous solution (at a concentration of 5×10^{-4} M) of the radical (XXXI) at different pH in the *X*-band (*a*), *Q*-band (*b*), and the 2-mm band (*c*) at 23 °C.[21]

observe the doublet splitting of two (in the *Q*-band) or all three (in the 2 mm range) components of the triplet (Fig.1) the EPR spectrum of the radical (XXXI). It has been shown[21] that the observed effect is associated with the protonation of the N(3) atom in the radical (XXXI) and with the difference between the HFI constants a_N and the *g*-factors of the Ṙ and $\dot{R}H^+$ forms.

This conclusion has been confirmed, firstly, by the similarity of the p*K* values for this radical measured potentiometrically and by EPR.[61] The dependence of the function $f = I_{RH^+}/(I_R + I_{RH^+})$ (I_{RH^+} and I_R are the intensities of the EPR signals of the $\dot{R}H^+$ and Ṙ forms respectively) on the pH was used to determine the p*K* by the EPR method (Fig.2). Previously this function had been employed[62] to describe the distribution of the radical (I) between the aqueous and lipid phases:



Secondly, the HFI constants and the *g*-factor of the radical (XXXI) in the $\dot{R}H^+$ form are close to the corresponding values for the imidazolinium salt (XXXIV) (Table 1). Thirdly, the effect of pH on the EPR spectra of the radicals (I) and (XXXIV), in which the N(3) atom capable of being protonated is absent, has not been observed.

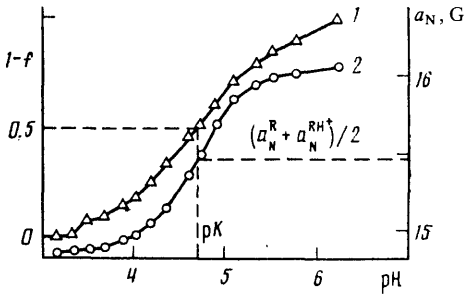


Figure 2. The pH dependence of the function $I-f = I_R/(I_R + I_{RH^+})$ (curve *1*) and of the HFI constant a_N (curve *2*) for the radical (XXXI).[61]

3. Proton Exchange in Nitroxy-radicals of the Imidazoline and Imidazolidine Types

(a) Manifestation of the protonation of the N(3) atom in radicals of the imidazoline and imidazolidine types in EPR spectra. The influence of pH on the EPR spectra of one of the radicals—an imidazolidine derivative (XXXI)—is illustrated in Fig.1.[21] In the pH range 3.5–6, the high-field component of the EPR spectrum in the *X*-range (Fig.1*a*) is split into two resolved components, whose relative intensities vary reversibly with pH. This form of the spectrum has been explained by the superposition of two triplet EPR spectra differing in the HFI constants and *g*-factors. Indeed, the use of spectrometers with a higher working frequency made it possible to

The p*K* found by the EPR method, the HFI constants, and the *g*-factors are listed in Table 1 for a series of radicals of the imidazoline and imidazolidine types.

The EPR spectrum of the radicals (XXXI) and (XXXIII) with $pK > 3$ in the region where $pH \simeq pK$ represents a superposition of the spectra of the Ṙ and $\dot{R}H^+$ forms of the radical, which is due to the slow $\dot{R} \rightleftarrows \dot{R}H^+$ exchange.[61] In this case, the p*K* of the radicals were determined using the pH dependence of *f* (Fig.2). It is noteworthy that the p*K* of the radicals determined in this way can differ in general from the true values as a consequence of the different widths of the high-field components of the spectra of the Ṙ and $\dot{R}H^+$ forms. However, for the radicals investigated (Table 1), these differences are small ($\lesssim 5\%$) and can lead to an error not greater than 0.1 in the measurement of the p*K*. In the *X*-range, the pH

dependence of the quantity a_N (Fig.2), measured as the distance between the first and second components of the triplet, can be used together with the functions f for the determination of the pK of the radical; here $a_N(pK) = (a_N^{\dot{R}H^+} + a_N^{\dot{R}})/2$ ($a_N^{\dot{R}H^+}$ and $a_N^{\dot{R}}$ are the HFI constants for the $\dot{R}H^+$ and $\dot{R}$ forms respectively). Two resolved signals in the third component of the EPR spectrum were not observed for the radicals (XXXII) and (XXXV) in the pH $\simeq$ pK region. The change in pH led to a reversible change in the parameters of the triplet EPR spectra of these radicals, namely the HFI constant and the g-factor, which can be explained by the rapid proton exchange $\dot{R} \rightleftarrows \dot{R}H^+$. In this case, the p$K$ of the radical can be calculated from the conditions leading to agreement between the experimental curve and the curve calculated by Eqn.(11) and also from the condition

$$a_N(pK) = (a_N^{\dot{R}H^+} + a_N^{\dot{R}})/2.$$

Table 1. The pK values, found by EPR, the calculated and experimental HFI constants a_N, and the g-factors for the $\dot{R}$ and $\dot{R}H^+$ forms of certain radicals of the immidazoline and imidazolidine types.[21,61,63]

Radical	pK (±0,1)	g-Factor* (±0.0001)		a_N (±0.05), G	
		$\dot{R}H^+$	$\dot{R}$	$\dot{R}H^+$	$\dot{R}$
(XXXI)	4.7	2.0057 2.0046**	2.0054 2.0044**	14.85 6.03**	16.10 7.29**
(XXXII)	1.3	2.0057 2.0047	2.0055 2.0037**	14.95 5.74** 10.22***	15.85 7.22** 11.22***
(XXXIII)	6.1	2.0057 2.0048	2.0054 2.0036	15.05 5.73**	15.80 7.26**
(XXXIV)	—	2.0057 2.0047**	—	14.80 5.78**	—
(XXXV)	0.8	2.0057 2.0046**	2.0054 2.0036**	15.00 5.79**	15.85 7.24**

* The experimental g-factors, determined by Khramtsov and coworkers,[21,61] are displaced relative to the tabulated values by the constant amount $\Delta g = 6 \times 10^{-4}$ as a consequence of a systematic apparatus error.

** Calculated values (without allowance for solvation effects).[61]

*** Calculated values (with allowance for solvation effects).[64]

As can be seen from Table 1, when the N(3) atom is protonated, the changes in the g-factor are $(2-3) \times 10^{-4}$ and those in the HFI constant are 0.8 – 1.2 G. Additional evidence for the possibility of such large changes in the parameters of the EPR spectra of NR of the imidazoline and imidazolidine types on protonation of the N(3) atom has been obtained by quantum-chemical methods.[61]

(b) Quantum-chemical calculations of the HFI constants and g-factors of radicals of the imidazoline and imidazolidine types in the protonated and non-protonated forms. Quantum-chemical calculations of the electronic structures of the radicals have been carried out[61] by the restricted and unrestricted Hartree – Fock methods in terms of the INDO approximation.[65] In the calculation of the g-factor by the restricted Hartree – Fock method, the molecular orbitals were calculated by Stone's method.[66] The available experimental data for the geometries of the analogous imidazoline radicals with the N-oxide linkage were used for the radicals (XXXII) – (XXXV).[67] In the calculation of the electronic structure of the radical (XXXI), the geometry of the corresponding hydroxypyrrolidine was attributed to the latter.[68]

The constants for the HFI with the N(1) atom (a_N) and the g-factors for the above radicals, calculated theoretically and found experimentally,[61] are compared in Table 1. The calculated constants a_N differ appreciably from the experimental values owing to the approximate nature of the INDO method used in the calculation.[65] However, the characteristics of the changes in the HFI constants on passing from uncharged to charged forms are reproduced quite satisfactorily. In these radicals, the spin density is localised mainly on the N – O· π orbital ($\rho_N^\pi \simeq 0.31$; $\rho_O^\pi \simeq 0.67$). When the N(3) atom is protonated, the splitting of the levels of the π orbitals of the N and O atoms increases under the influence of the field of the positive charge and the relative electronegativity of the oxygen atom diminishes: as a result of this, the antibonding orbital of the unpaired electron is localised to a greater extent on the oxygen atom and to a lesser extent on the nitrogen atom ($\rho_N^\pi = 0.26$; $\rho_O^\pi = 0.72$). The sum $\rho_N^\pi + \rho_O^\pi$ then remains almost constant. Since the constant a_N is linked to the π-electron spin populations by relations of the type[65] $a_N = Q_N^N \rho_N^\pi + Q_O^N \rho_O^\pi$, where $Q_N^N > 0$ and $Q_O^N < 0$, the above redistribution of spin density on protonation of the N(3) atom does in fact diminish the constants a_N.

The values of a_N for the $\dot{R}$ and $\dot{R}H^+$ forms of the radical (XXXII) have been calculated recently[64] taking into account solvation within the framework of a solvate model.[69] As can be seen from Table 1, allowance for solvation ensures the best agreement between the calculated and experimental values of a_N with retention at the same time of the difference between the a_N for the two forms of the radical, amounting to 1 G.

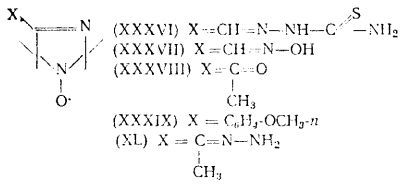
It follows from Table 1 that, in agreement with experiment, the g-factors of the protonated radicals are close to one another and do not differ from the g-factor of the imidazolinium salt (XXXIV). The non-protonated radicals are also characterised by a similar g-factor [with the exception of the radical (XXXI), whose geometry has been estimated tentatively by Khramtsov et al.[61]]. The g-factors of the protonated radicals are appreciably greater than those of the non-protonated radicals.

Analysis of the calculated data has shown that this increase in the g-factors is caused mainly by the increase in the component of the g-tensor $\Delta g_{zz} = 0.0034$ corresponding to the direction of the N – O· bond. The main contribution to this component ($\Delta g_{zz} = 0.0042$) comes from the transition from the molecular orbital corresponding approximately to the orbital of the unshared electron pair of oxygen n to the orbital of the unpaired electron $\pi\uparrow$, whose admixture in the ground state is determined mainly by the spin – orbital interaction at the oxygen atom.

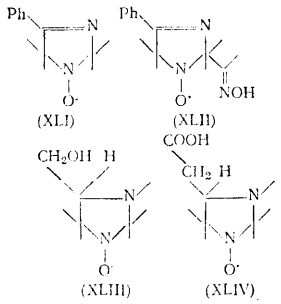
The above analysis has confirmed that the effects associated with the protonation of the N(3) atom can induce changes in the constants a_N and in the g-factor, which have been observed experimentally, and thus serves as yet another confirmation of the validity of the assignment of the EPR spectra by Khramtsov et al.[61]

(c) The equilibrium constants of the proton exchange in radicals and their relation with the character of the frequency exchange in the EPR spectra. The influence of the protonation of the N(3) atom on the EPR spectra of a large series of radicals of the imidazoline and imidazolidine types has been investigated.[51] Table 2 presents the pK,

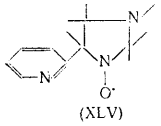
the HFI constants, and the *g*-factors for the radicals (XXXVI)–(LI) in the protonated and deprotonated forms found by EPR and also indicates the character of the $\dot{R} \rightleftarrows \dot{R}H^+$ exchange.



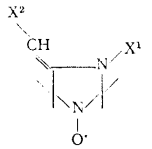
(XXXVI) X = CH=N–NH–C(=S)–NH$_2$
(XXXVII) X = CH=N–OH
(XXXVIII) X = C(=O)–CH$_3$
(XXXIX) X = C$_n$H$_{2n}$–OCH$_3$-*n*
(XL) X = C(CH$_3$)=N–NH$_2$



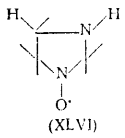
(XLI) (XLII) (XLIII) (XLIV)



(XLV)

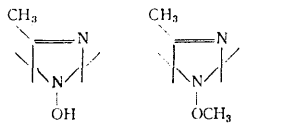


(XLVII) X^1 = H X^2 = NO$_2$
(XLVIII) X$_1$ = H X^2 = C(=O)–CH$_3$
(XLIX) X^1 = H X^2 = C(=O)–(CH$_2$)$_4$–COOH
(L) X^1 = CH$_3$ X^2 = C(=O)–CH$_2$–N
(LI) X^1 = CH$_3$ X^2 = C(=O)–CH$_2$I



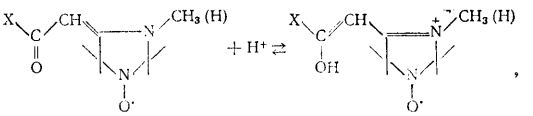
(XLVI)

The protonation of the N(3) atom in the given radicals is accompanied by appreciable changes in the HFI constants a_N (Δa_N = 0.8 to 1.3 G) and in the *g*-factor [$\Delta g = (2-3) \times 10^{-4}$]. The values of p$K$ for the imidazoline radicals correspond to the region of low pH values [pK < 3, with the exception of the radical (XXXIII), which has pK = 6.1]; they are smaller than the pK of the imidazolidine radicals [pK = 3.0–4.7 for the radicals (XXX), (XXXI), and (XLIII)–(XLVI)]. The smaller pK of the radicals compared with the pK of the corresponding diamagnetic molecules of imidazolines and imidazolidines[19,51] have been explained by the electron-accepting influence of the nitroxy-group. Indeed, pK = 1.9 for the radical (XXXII), which is appreciably less than the pK of the corresponding diamagnetic analogues (LII) and (LIII):[61]



(LII), pK = 3.85 (LIII), pK = 3.85

We may also note that pK = 11.15 for the =NOH group in the radical (XLII) [cf. the radical (XIII)] and pK = 2.0 for the COOH group in the radical (XLIV) [cf. the radical (XV)] [51] have been found by EPR. The high pK = 7.8, found by EPR for the imidazolidine radical (XLVII), is associated with its deprotonation in the 3-position. The deprotonation of this radical has been demonstrated chemically.[70] The deprotonation in the 3-position is also responsible for the change in the EPR spectra of the imidazolidine radicals (XLVIII) and (XLIX) in an alkaline medium (Table 2).[51] For the radicals (XLVIII) and (XLIX), yet another pK has been observed (Table 2) in the region of low pH values, which, as for the radicals (L) and (LI), has been explained by the protonation of the enamino-keto-group. It is known that the vast majority of enaminoketones are protonated at the oxygen atom.[71,72] The protonation of the radicals (XLVIII)–(LI) at the oxygen atom is described by the equation



(15)

where X are substituents. The positive charge on the $\dot{R}H^+$ form is then mainly localised at the N(3) atom, which explains the similarity of the values of Δa_N and Δg for the protonation of the radicals (XLVIII)–(LI) and of the N(3) atom in radicals of the imidazolidine type (Table 2).

Table 2. The values of pK, a_N, and *g*-factors for the $\dot{R}$ and $\dot{R}H^+$ forms of certain radicals of the imidazoline and imidazolidine types as well as the character of the $\dot{R} \rightleftarrows \dot{R}H^+$ frequency exchange.[51,63]

Radical pK (±0.1)		*g*-Factor (±0.0001)		a_N (±0.02), G		Character of exchange
		$\dot{R}H^+$	$\dot{R}$	$\dot{R}H^+$	$\dot{R}$	
(XXX)	3.0	2.0057**	2.0054**	14.85	16.20	s
(XXXVI)	−0.2	2.0057	2.0055	14.80	15.36	r
(XXXVII)	0.1	2.0057	2.0055	14.85	15.64	r
(XXXVIII)	0.2	2.0057	2.0055	14.93	15.81	r
(XXXIX)	1.2	2.0057**	2.0054**	15.00	15.85	r
(XL)	2.5	2.0057	2.0055	15.03	15.77	i
(XLI)	0.6	2.0057	2.0055	14.95	15.65	r
(XLII)	1.0	2.0058	2.0057	14.69	15.13	r
(XLII)	11.15	2.0057	2.0056	15.12	15.35	–
(XLIII)	3.85	2.0057	2.0055	14.89	15.96	s
(XLIV)	2.0	2.0058	2.0058	14.60	14.76	–
(XLIV)	4.3	2.0058	2.0055	14.76	15.92	s
(XLV)	4.5	2.0057	2.0055	14.72	15.89	s
(XLVI)	4.35	2.0057	2.0055	15.02	16.18	s
(XLVII)	7.8	2.0056	2.0055	15.29	15.75	s
(XLVIII)	1.1	2.0057	2.0056	15.03	15.46	r
(XLVIII)	13.25	2.0056	2.0055	15.47	15.98	r
(XLIX)	1.0	2.0057	2.0056	15.03	15.47	r
(XLIX)	13.5	2.0056	2.0065	15.46	15.92	r
(L)	−0.7	2.0058	2.0055	14.20	15.41	s
(LI)	0.2	2.0058	2.0055	14.40	15.57	s

*r = rapid, i = intermediate, and s = slow (in terms of the EPR time scale).
**See first footnote to Table 1.

The relation between the character of the $\dot{R} \rightleftarrows \dot{R}H^+$ exchange and the pK of the radical has attracted attention: for radicals with pK > 3 and also for the radicals (XLVIII) and (XLIX) with pK = 13.25 and 13.5 respectively, a rapid exchange has been observed, while in the case of the radicals with pK = 3–8 a slow exchange has been observed (Table 2). This has been explained in two investigations.[51,61] In aqueous solutions, the proton exchange between the $\dot{R}$ and $\dot{R}H^+$ forms is described by two mechanisms:

$$\dot{R} + H^+ \underset{k_{-1}^{H^+}}{\overset{k_1^{H^+}}{\rightleftarrows}} \dot{R}H^+; \qquad (16)$$

$$\dot{R}H^+ + OH^- \underset{k_{-1}^{OH^-}}{\overset{k_1^{OH^-}}{\rightleftarrows}} \dot{R} + H_2O\,. \qquad (17)$$

The condition for slow exchange requires that the reciprocals of the lifetimes of the radicals in the $\dot{R}$ and $\dot{R}H^+$ forms ($1/\tau_R$ and $1/\tau_{RH^+}$ respectively) should be appreciably smaller than the difference between the frequencies of the EPR signals of these forms $\Delta\omega$:

$$1/\tau_R,\ 1/\tau_{RH^+} \ll \Delta\omega \qquad (18)$$

For the mechanism (16), which is the main one in an acid medium, we have

$$1/\tau_{RH^+} = k_{-1}^{H^+} = k_1^{H^+}K_a = k_1^{H^+} \times 10^{-pK},$$
$$1/\tau_R = k_1^{H^+}[H^+] = k_1^{H^+} \times 10^{-pH}, \qquad (19)$$

where $K_a = k_{-1}^{H^+}/k_1^{H^+}$ is the equilibrium constant of reaction (16) (by definition $K_a = 10^{-pK}$). For the mechanism (17), which is the main one in an alkaline medium, we have

$$1/\tau_{RH^+} = k_1^{OH^-}[OH^-] = k_1^{OH^-} \times 10^{pH-14}, \qquad (20)$$
$$1/\tau_R = k_1^{OH^-} \times 10^{pK-14}.$$

On substituting Eqns.(19) and (20) in Eqn.(18), we obtain the condition for slow exchange:

$$\lg(k_1^{H^+}/\Delta\omega) < pK,\ pH < 14 - \lg(k_1^{OH^-}/\Delta\omega)\,. \qquad (21)$$

For diffusion-controlled proton exchange reactions, $k_1^{H^+} \simeq k_1^{OH^-} \simeq 10^{10}$ litre mol^{-1} s^{-1} [1] and $\Delta\omega \simeq 10^7$ s^{-1} for the protonation of the N(3) atom (Fig.2). On substituting the values of $k_1^{H^+}$, $k_1^{OH^-}$, and $\Delta\omega$ in Eqn.(21), we obtain the condition for the slow frequency exchange in the EPR spectra for diffusion-controlled proton exchange reactions:[61]

$$3 < pK < 11\,. \qquad (22)$$

This condition is satisfactorily consistent with the available experimental literature data. Indeed, for the radicals (III),[46] (XXVIII),[19] (XXXII), (XXXV)–(XXXIX), (XLI), and (XLII) [51] with $pK < 3$, the hydroxynitroxy-radical ($pK = 12.96$),[32] a series of alcohol radicals,[28] and the radicals (XLVIII) and (XLIX) [51] with $pK > 11$, a rapid $\dot{R} \rightleftarrows \dot{R}H^+$ proton exchange was observed. For the radicals (VI)–(VIII),[48] (XXX), (XXXI), (XXXIII),[62] (XLIII), (XLIV), (XLV), and (XLVII) [51] with pK in the range $3 < pK < 11$, a slow exchange was observed. Finally, for the radical (XL) [51] ($pK = 2.5$) and the radicals $CH_3\dot{C}HOH$ ($pK = 11.51$) and $(CH_3)_2\dot{C}OH$ ($pK = 12.03$),[28] the character of the exchange is intermediate. On the other hand, the rapid $\dot{R} \rightleftarrows \dot{R}H^+$ frequency exchange in the EPR spectra of the radical (XXIX) ($pK = 4.5$) [19] and the slow exchange in the EPR spectra of the radicals (L) ($pK = -0.7$) and (LI) ($pK = 0.2$),[51] conflict with condition (22). In order to account for these findings in conformity with condition (21), it is essential to postulate that $k_1^{H^+} \gg 10^{10}$ litre mol^{-1} s^{-1} for the radical (XXIX) (i.e. $k_1^{H^+} \simeq 10^{11}$ litre mol^{-1} s^{-1}) and $k_1^{H^+} \ll 10^{10}$ litre mol^{-1} s^{-1} (smaller by 3–4 orders of magnitude or more) for the radicals (L) and (LI). Appreciably lower bimolecular protonation constants $k_1^{H^+}$ compared with the corresponding value for diffusion-controlled reactions have been noted in the literature, for example for CH acids.[1] As mentioned above, the enaminoketo-group in the radicals (L) and (LI) is apparently protonated at the oxygen atom in accordance with Eqn.(15). The redistribution of electron density occurring under these conditions can lead to an appreciable increase in the activation energy for the chemical reaction and hence to a decrease in $k_1^{H^+}$. It is also possible that a decrease in the constants $k_1^{H^+}$ for the radicals (L) and (LI) can be explained by steric hindrance.[51]

(d) Kinetic characteristics of the reactions. The appreciable difference between the parameters of the EPR spectra of the $\dot{R}$ and $\dot{R}H^+$ forms of the imidazoline and imidazolidine radicals (Tables 1 and 2) enabled us[73,74] to propose a new approach to the study of the kinetics of proton exchange reactions by EPR. For the intermediate $\dot{R} \rightleftarrows \dot{R}H^+$ frequency exchange, all the parameters characterising the kinetics of the proton exchange reaction are susceptible to determination by EPR: the rate constants, the activation energies, and the kinetic isotope effects.[61,73,74]

According to Eqn.(22), the intermediate exchange should be observed for radicals with $pK \simeq 3$ and $pK \simeq 11$; among the radicals investigated (Tables 1 and 2), this condition is satisfied by the radicals (XXX) with $pK = 3.0$ and (XL) with $pK = 2.5$. Indeed, for $pH \simeq pK$, the high-field component of the radical (XL) is broadened as a result of the $\dot{R} \rightleftarrows \dot{R}H^+$ exchange.[72] In the case of tha radical (XXX), for increased temperatures spectral changes characteristic of the transition from slow to intermediate exchange are also observed.[61] In conformity with Eqn.(22), such spectral changes with increase in temperature have not been noted for the radical (XXXI) with $pK = 4.7$.

In order to determine the lifetimes τ_R and τ_{RH^+} and the corresponding proton exchange rate constants $k_1^{H^+}$ and $k_{-1}^{H^+}$, the high-field component in the EPR spectra of the radicals (XXX) and (XL) was modelled on a computer.[61,74] In calculating the spectra, use was made of Eqn.(22), describing the line shape of the EPR signal for rapid exchange involving two positions; the unresolved superhyperfine structure was taken into account in two ways: (a) by the direct allowance for the HFI with the methyl protons, whose contribution to the non-uniform broadening of the EPR signal is decisive,[61] and (b) by representing the form of the spectral line by a composite function comprising one calculated by Eqn.(2) and the Gaussian distribution function[73,74] [this is based on the insignificant difference ($\lesssim 5\%$) between the width of the Gaussian distributions in the $\dot{R}$ and $\dot{R}H^+$ forms of the radicals investigated (see also Lebedev and Muromtsev[75])].

The bimolecular protonation constants $k_1^{H^+}$ for the radical (XL), amounting to $3 \times 10^9 - 10^{10}$ litre mol^{-1} s^{-1} (Fig.3) in the experimental temperature range (274–300 K), are appreciably greater than for the radical (XXX) ($k_1^{H^+} \simeq 5 \times 10^8$ litre mole^{-1} s^{-1} at 20 °C); under these conditions, the temperature dependence of τ_R and τ_{RH^+} can be described by a linear function in terms of the Arrhenius parameters and, according to Eqn.(19), we have

$$k_1^{H^+} = 1{,}6 \cdot 10^{14} \exp(-5800/RT),\ \text{litre mol}^{-1}\,\text{s}^{-1};$$
$$k_{-1}^{H^+} = 1{,}0 \cdot 10^{14} \exp(-8900/RT),\ \text{s}^{-1}. \qquad (23)$$

The high activation energy for the protonation of the radical ($\Delta E = 5.8 \pm 0.4$ kcal mol^{-1}) may indicate non-diffusional control of the reaction.

The possibility of obtaining quantitative information about the isotope effects in proton exchange reactions using pH-sensitive NR is of interest. A difference has been observed[74] between the EPR spectra of the radical (XL) in H_2O and D_2O (Fig.3). Therefore, in D_2O the temperature dependence of the lifetimes of the radical in the $\dot{R}$ and $\dot{R}D^+$ forms can also be described by a linear function in terms

of the Arrhenius parameters and the rates of the forward and reverse exchange reactions can be formulated as follows:

$$k_1^{D^+} = 9{,}9 \cdot 10^{13} \exp(-6100/RT), \text{ litre mol}^{-1}\text{ s}^{-1};$$
$$k_{-1}^{D^+} = 9{,}7 \cdot 10^{13} \exp(-10\,000/RT), \text{ s}^{-1}. \quad (24)$$

Comparison of Eqns.(23) and (24) shows that, for the given reaction, both thermodynamic (different equilibrium constants) and kinetic (different rate constants) isotope effects are observed. The thermodynamic isotope effect $\Delta pK = pK^{D_2O}/pK^{H_2O} = 0.4$ (at $T = 294$ K). This agrees with the fact that, for the majority of ionising groups, the pK corresponding to ionisation via the loss of a deuteron in D_2O are higher by $\sim 0.4-0.6$ of a unit than the pK for the ionisation of the same groups via the loss of a proton in H_2O.[76] The kinetic isotope effect has the usual value for reactions of this type ($k_1^{H^+}/k_1^{D^+} = 2.7 \pm 0.2$ and $k_{-1}^{H^+}/k_{-1}^{D^+} = 6.9 \pm 0.4$ at $T = 294$ K) and in order to account for it there is no need to resort to tunnelling effects.[5,6] This conclusion is confirmed by the satisfactory validity of the Arrhenius relation for k_1 (Fig.3). We may note that, in the case of the radical (XXX), where the interaction between the N(3) atom and the proton is additionally hindered by the presence of the bulky CH_3 group, the Arrhenius relation does not hold for k_1,[61] the rate constant k_1 being an order of magnitude smaller than for the radical (XL) (Table 3). Naturally the determination of the contribution of tunnelling on the basis of the temperature variation of the constant k_1 requires the measurement of the latter over a wider temperature range. Unfortunately, the proton exchange frequencies can be measured by EPR only when they are close to the difference between the Zeeman frequencies of the protonated and non-protonated forms of the radical, which limits the temperature range for the measurement of k_1 for the radicals (XXX) and (XL) to $\Delta T \simeq 40$ K.[61,74] We may point to the possibility, in principle, of extending the range of measurement of the proton exchange frequencies by EPR involving the use of spectrometers with different working frequencies. As can be seen from the EPR spectra of the radical (XXXI) presented in Fig.1, the difference between the frequencies of the $\dot{R}$ and $\dot{R}H^+$ forms in the X, Q, and 2 mm bands is significantly different (by a factor of ~ 4).

Table 3. The rate constants for the forward (k_f) and reverse (k_r) proton exchange reactions of certain radicals with the compounds BH^+ at 21 °C.[74]

Radical	BH+	$10^{-7}\,k_f$, litre mol^{-1} s^{-1}	$10^{-7}\,k_r$, litre mol^{-1} s^{-1}
(XL)	H_3O^+	850±90	2.7±0.3*
(XXX)	H_3O^+	50	0.05*
(XLVI)	CH_3COOH	20±1.5	53±3
(XXXI)	CH_3COOH	9.3±0.6	9.3±0.6
(XXXIII)	$H_2PO_4^-$	20±2	200±20

* The constant is expressed in s^{-1}.

Thus the EPR method makes it possible to determine all the kinetic parameters of the proton exchange reactions in nitroxy-radicals. However, this method is significantly limited, since it is applicable only to reactions in radicals with $pK \simeq 3$ and $pK \simeq 11$.

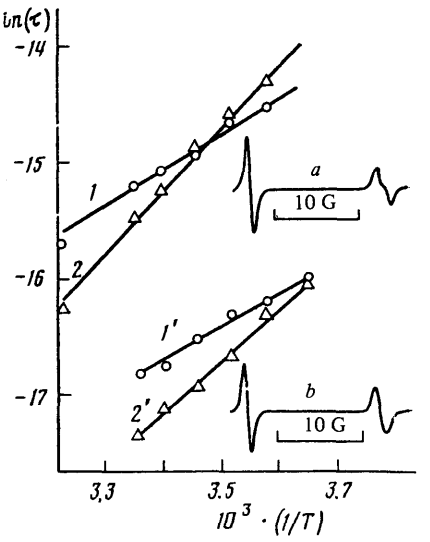


Figure 3. EPR spectra of 5×10^{-5} M solutions of the radical (XL) (the central and high-field components) at 278 K in D_2O (*a*) and H_2O (*b*); temperature variation of the lifetimes τ_R (line *1*) and τ_{RD^+} (line *2*) in D_2O and τ_R (line *1'*) and τ_{RH^+} (line *2'*) in H_2O.[74]

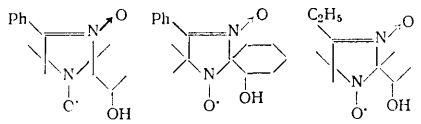
The methodological approach permitting an increase in the rate of the $\dot{R} \rightleftarrows \dot{R}H^+$ exchange without raising the temperature is therefore very useful for stable nitroxy-radicals.[73,74] Previously[30,31] this approach was realised for short-lived radicals by adding to the aqueous solution a buffer with pK_{buf} close to the pK of the radical, as a result of which reaction (7b) becomes the principal exchange mechanism. The influence of the buffer concentration on the rate of exchange has been investigated[73,74] for a series of pH-sensitive stable NR with $3 < pK < 11$, where a slow exchange is observed in the absence of a buffer. An increase in the buffer concentration led to spectral changes characteristic of the transition from the slow to the intermediate exchange and then to rapid exchange (Fig.4). In the region of the intermediate exchange, the lifetimes of the radicals τ_R and τ_{RH^+} and the corresponding rate constants k_f and k_r were calculated by modelling the EPR spectra (Table 3). Table 3 presents the rate constants for the forward and reverse proton exchange reactions of certain radicals with different partners. A correlation has been observed between the bimolecular protonation constant and the steric accessibility of the N(3) atom: in the exchange with a solvated proton in the radicals (XL) and (XXX), which have similar pK, the protonation constant is more than an order of magnitude smaller for the radical (XXX), which has the bulky CH_3 group at the N(3) atom; the replacement of the hydrogen atom at the N(3) atom in the radical (XLVI) by the CH_3 group [in the radical (XXXI)] also leads to a significant decrease in the bimolecular protonation constant in the proton exchange reaction with an acetic acid molecule.

Thus the EPR method is extremely effective in the study of the kinetics and thermodynamics of proton exchange reactions in solutions. The presence of an unpaired electron in the radical does not influence the rate of the chemical proton transfer reaction and makes it possible to follow it by EPR, which creates the possibility of using the proton exchange reactions in NR as model processes in

the study of various factors (the structure of the radical and the properties of the solvent) influencing the proton transfer. It is important to note that the organic chemistry of NR has been well developed and ensures the availability of different NR.[18,22]

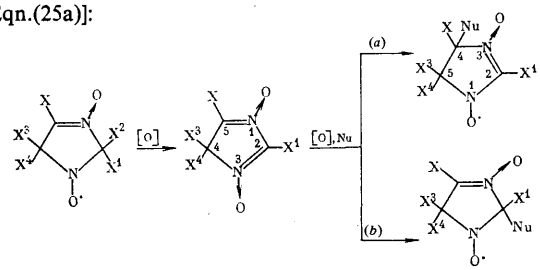
4. Proton Exchange in Nitronylnitroxy- and Iminonitroxy-radicals

(a) The transformations of 3-imidazoline 3-oxide nitroxy-radicals into nitronylnitroxy-radicals as a consequence of a change in pH. In the study of the influence of pH on the EPR spectra of stable 3-imidazoline 3-oxide radicals (LIV)–(LVI) with a hydroxyalkyl group in the 2-position in the heterocycle, it was observed unexpectedly[77,78] that at pH > 12 the spectra of aqueous solutions of these radicals are transformed irreversibly into more complex multiplet spectra typical of NNR:[46,79]



(LIV) (LV) (LVI)

It has been shown[77,78] that in this case the 3-imidazoline 3-oxide NR are indeed converted into NNR in accordance with a general scheme involving the intermediate formation of 4*H*-imidazole *N*-oxides [Eqn.(25a)]:



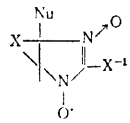
(25)

This reaction leads to extensive possibilities for the synthesis of new NNR; here it is possible to vary both the substituents X–X[4] and the nucleophile Nu (Nu = OH^-, OCH_3^-, NH_3, etc.) as a function of the reaction medium.

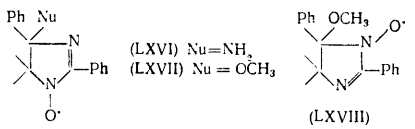
According to Eqn.(25b), nucleophilic attack can be directed not only to the 5-position in 4*H*-imidazole di-*N*-oxide, with formation of a NNR, but also to the 2-position, with formation of new 3-imidazoline 3-oxide NR.

By reducing with triphenylphosphine the NNR obtained by reaction (25a),[46] a series of new 3-imidazoline 3-oxide NR with a substituent (Nu) other than an alkyl substituent at C(2) (Nu = OCH_3 or NH_2) as well as INR have been obtained.[78,80]

Table 4 presents the parameters of the EPR spectra of a series of NNR and INR obtained in accordance with Scheme (25).



	(LXVII)	(LXVIII)	(LIX)	(LX)	(LXI)	(LXII)	(LXIII)	(LXIV)	(LXV)
Nu	OH	OH	OH	OH	NH_2	NH_2	OCH_3	OCH_3	OCH_3
X	Ph	Ph	Ph	C_2H_5	Ph	Ph	Ph	Ph	Ph
X^1	CH_3	$(CH_2)_4CHO$	Ph	CH_3	$(CH_2)_4CONH_2$	Ph	CH_3	$(CH_2)_4COOCH_3$	Ph



(LXVI) Nu=NH_2
(LXVII) Nu = OCH_3

(LXVIII)

Comparison of the HFI constants for the NNR (LVII) and (LVIII) with the corresponding values for radicals enriched in the ^{15}N isotope at N(3) made it possible to assign unambiguously the "nitrogen" HFI constants to the nuclei of the N(1) and N(3) atoms (Table 4).

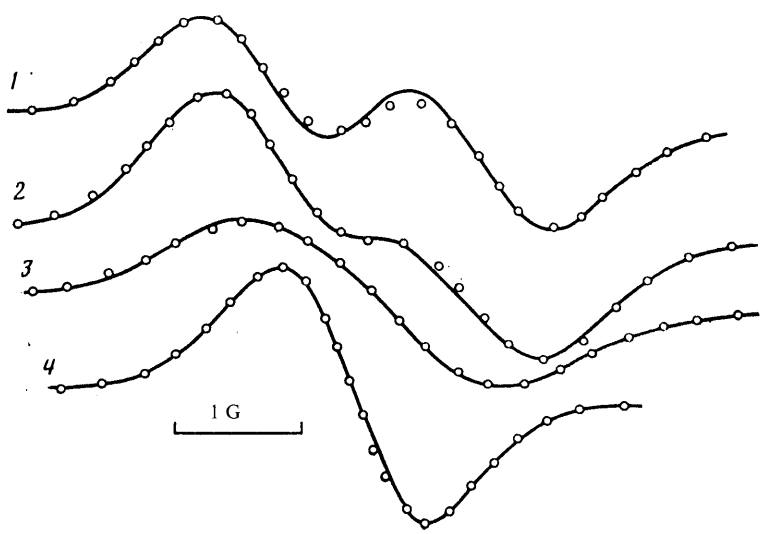


Figure 4. The high-field component of the calculated (circles) and observed (continuous lines) EPR spectra of a 5×10^{-5} M solution of the radical (XLVI) in the potassium acetate buffer (pH 4.35) at 294 K and different buffer concentrations (M): 1) 0; 2) 2.27×10^{-2}; 3) 5.76×10^{-2}; 4) 0.28.[74]

(b) The influence of pH on the EPR spectra of NNR and INR. Table 4 shows that the parameters of the EPR spectra of a series of NNR and INR change as the pH is varied, which has been explained by the protonation of NH_2 or the deprotonation of the OH group at the C(4) atom.[77,78] On the other hand, the EPR spectra of the NNR (LVIII)–(LXV) and the INR (LXVII) and (LXVIII), in the structure of which there are no such groups at C(4) capable of being protonated, did not change in the pH range 1–13.

The EPR spectra of the NNR (LVII)–(LX) in the pH range close to the pK represent a superposition of the spectra of the radicals and the deprotonated form; here p$K \simeq 9.2$ for the OH group in the radicals (LVII)–(LX).[78]

Table 4. The HFI* constants for a series of NNR and INR in H_2O (in gauss).[77,78]

Radical	pH > pK + 1.5					pH < pK − 1.5				
	$a_{N(1)}$	$a_{N(3)}$	a_H	$a_{N(NH_2)}$	$a_{H(OCH_3)}$	$a_{N(1)}$	$a_{N(3)}$	a_H	$a_{N(NH_3^+)}$	$a_{H(OCH_3)}$
(LVII)	8.67	8.28	3.13	—	—	8.00	8.00	3.13	—	—
(LVII)**	8.67	11.65	3.13	—	—	8.00	11.34	3.13	—	—
(LVIII)	8.73	8.22	1.93	—	—	8.00	8.00	1.93	—	—
(LVIII)**	8.73	11.57	1.93	—	—	8.00	11.35	1.93	—	—
(LIX)	8.50	8.00	—	—	—	7.93	7.93	—	—	—
(LX)	8.75	8.45	3.17	—	—	8.13	8.13	3.17	—	—
(LXI)	8.00	8.00	1.90	—	—	7.55	7.55	1.90	1.2	—
(LXII)	8.05	8.05	—	0.2	—	7.60	7.60	—	1.2	—
(LXIII)	7.68	7.52	1.80	—	0.60	7.68	7.52	1.80	—	0.60
(LXIV)	7.70	7.50	1.30	—	0.55	7.70	7.50	1.30	—	0.55
(LXV)	7.67	7.67	—	—	—	7.67	7.67	—	—	—
(LXVI)	9.26	4.27	—	0.5	—	8.37	3.9	—	1.6	—
(LXVII)	9.10	4.10	—	—	—	9.10	4.10	—	—	—
(LXVIII)	8.90	4.00	—	—	—	8.90	4.00	—	—	—

*The accuracy of the determination of the constants is to within 0.05 G.

The radicals (LXVII)* and (LXVIII) are the radicals (LXVII) and (LXVIII) respectively enriched in the ^{15}N isotope at N(3).

The lines in the EPR spectra of the NNR (LXI)–(LXII) initially broaden as the acidity of the medium increases to pH < 3 and beyond and are then split into three components with the intensity ratios 1 : 1 : 1.[78] The observed spectral changes have been explained by the rapid proton exchange in the given radicals and also by the significant increase in the constant for the HFI with the nitrogen nucleus of the NH_2 group when the latter is protonated. Since the relaxation time of the nuclear spin of nitrogen is high compared with the EPR time scale, in describing the experimental spectrum one may assume that proton exchange takes place between the $\dot{R}$ and $\dot{R}H^+$ forms of the radical with the same projection of the nuclear spin of nitrogen S_z^N. Thus, if the resonance frequencies of the $\dot{R}$ and $\dot{R}H^+$ forms of the radical are the same and equal to ω_0, then three lines for the following frequencies are observed in the EPR spectrum:

$$\bar{\omega}(S_z^N = 0, \pm 1) = (\omega_0 + S_z^N\delta_0)(1-f) + (\omega_0 + S_z^N\delta_+)f,$$

where f is the fraction of the $\dot{R}H^+$ form of the radical, δ_0 the HFI constant for the nitrogen of the NH_2 group, and δ_+ the HFI constant for the nitrogen of the NH_3^+ group. By modelling the central component of the EPR spectra of the radicals (LXI) and (LXII), the values of f at different pH were determined[78] and pK = 1.75 for the NH_2 group in these radicals was found.

The values p$K \simeq 9.2$ for the OH group in the radicals (LVII) to (LX) and p$K \simeq 1.75$ for the NH_2 group in the radicals (LXI) and (LXII) are smaller by approximately seven units than the pK of the corresponding aliphatic alcohols and amines,[81] which indicates a strong electron-accepting influence of the nitronylnitroxy-group. In conformity with this finding, deuterium exchange involving the methyl or methylene groups in the radicals (LVII) and (LVIII) is observed at pD $\gtrsim$ 12 in D_2O.[78]

It is essential to note that the character of the $\dot{R} \rightleftarrows \dot{R}H^+$ exchange in the NNR and INR investigated[77,78] is described by condition (22): in the radicals (LXI) and (LXII) with p$K \simeq 1.75$, the exchange is rapid, while in the radical (LXVI) with pK = 4.5 and in the radicals (LVII)–(LX) with p$K \simeq 9.2$ it is slow.

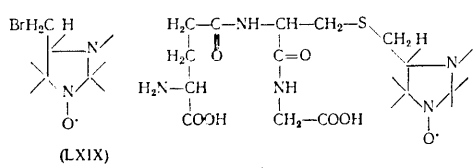
V. THE USE OF NITROXY-RADICALS AS pH PROBES

It follows from the preceding Sections that there are at present pH-sensitive NR which can be used as pH probes in the pH range 0–14. The measurement is then accurate to within 0.05 of a pH unit. This is especially important for biological systems including cell systems.[82,83]

1. Spin-labelled pH-Sensitive Proteins and Peptides

The spin-labelled pH-sensitive derivatives of the peptide hormone angiotension have been used[84,85] to study the conformational transitions and intramolecular interactions in the given octapeptide as a function of pH. The pH dependence of the EPR spectra of radical analogues of angiotensin containing NNR instead of the imidazole ring of histidine [similarly to the radical analogues of histidine (XXIII) and (XXIV)] has been investigated.[84] The observed spectral changes permitted the conclusion that an ion–dipole interaction takes place between the carboxylate ion and the C-end of the octapeptide and the nitronylnitroxy-ring. Such ion–dipole interaction promotes the stabilisation of the "loosened" structure of the hormone at neutral pH and its absence on protonation of the carboxy-group in an acid medium leads to a more compact "random" structure of angiotensin.[84] The above conformational transition has been recorded[85] from the change in the EPR spectra of the spin-labelled analogues of angiotensin, which the pH-sensitive radical (VI) was attached to the N-end, as a function of pH. It was concluded that the conformational transition is accompanied by the protonation of the amino-group at the N-end of the octapeptide.

When glutathione was modified by the radical (LXIX), a pH-sensitive spin analogue of the given tripeptide R-Glut was obtained:[63]



(LXIX) (*R*-Glut)

The parameters of the EPR spectrum of R-Glut in the pH range 1.5–4.5 varied to a much greater extent (Δa_N = 1.2 G, $\Delta g \simeq 0.0002$) than for the radical analogues of angiotensin ($\Delta a_N \lesssim 0.3$ G, $\Delta g \lesssim 0.0001$). This made it possible to use R-Glut as the pH-probe in the

study of the mechanism of proton transport through model biomembranes.[86,87]

We may note that the alkylating radical (LXIX) is capable of binding covalently to different functional groups of the aminoacid residues of proteins (SH, NH_2, NH [88]) with formation of macromolecular pH probes. In the solution of many biological problems, the possibilities involving the application of macromolecular spin pH probes are much greater than for the low-molecular-weight probes. A macromolecular probe of this kind has been obtained by modifying protein—human serum albumin—by the radical (LXIX).[61] The changes in the spectral parameters of the spin-labelled albumin in the pH range 1.7—4.7 (Δa_N = 1.15 G, $\Delta g \simeq 0.0002$) are due to the protonation of the N(3) atom of the radical ring and are not associated with the possible conformational transformations of the protein.

2. Proton Transport Through Model Phospholipid Membranes

Proton transport plays an important role in the regulation of a number of cell functions,[82,89] which has stimulated numerous investigations of the mechanisms of the transmembrane proton transfer.[90–100] In the study of proton transfer, through phospholipid vesicles, molecular pH probes are widely used; in most cases this is based on the possibility of inserting them into the inner volume within the vesicles (liposomes) and of recording with their aid the pH within the liposome (pH_{in}).[99,100] The change in the characteristics of the pH probe (fluorescence intensity,[99] the chemical shift of the ^{31}P NMR signal[100]) after a transmembrane pH gradient has been established makes it possible to measure the kinetics of the variation of pH_{in} and thus the proton fluxes across the membrane.

A spin pH probe (R-Glut) has been used to record the kinetics of the variation of the intraliposomal pH.[63,86,87] It was shown that R-Glut does not flow out of the inner volume within phosphatidylcholine (PC) monolamellar liposomes. When the pH in 0.1 M potassium citrate buffer is altered, a shift in the lines of the triplet EPR spectra of the R-Glut radical is observed without change in the line shape (rapid $\dot{R} \rightleftarrows \dot{R}H^+$ exchange); the high-field component then shifts to the greatest extent. For this reason, the intensity of the R-Glut spectrum at the frequency $\omega(pK)$ corresponding to the centre of the high-field component at pH = pK = 3.0 is a convenient parameter for the investigation of the kinetics of the variation of pH_{in}.

When a transmembrane pH gradient was created by altering the HCl concentration in the external volume relative to the PC liposomes, a change in the intensity $I(t)$ of the EPR spectrum of R-Glut was observed at a frequency $\omega(pK)$; when the sign of the HCl gradient was changed and its magnitude was reduced, the sign of the change in $I(t)$ was altered and its rate was diminished[63] (Fig.5). By analysing the initial section of the $I(t)$ kinetic curve, the derivative $(dI/dt)_{t=0}$ was determined, its value permitting the calculation of the proton flux j_{H^+} through a unit surface of the membrane in the initial instant after the pH gradient has been established. Table 5 presents the values of j_{H^+} following the creation of the same transmembrane pH gradient by varying the concentrations of different acids in the external volume relative to PC liposomes. The constancy of the EPR signal (over a period of ~2 h) in the case of the H_2SO_4 gradient in 0.1 M potassium citrate buffer shows that the electrically non-compensated proton transport, the K^+-dependent proton transport, and the transport of H^+ in the form of an undissociated citric acid molecule are slow processes and that their contribution to the observed $I(t)$ relations in the presence of HCl, $HClO_4$, and HNO_3 concentration gradients may be disregarded. The changes in $I(t)$ in the cases indicated are therefore determined by the anion- or X^--dependent transport of H^+ (X^- = Cl^-, ClO_4^-, or NO_3^-) or(and) the transport of protons in the form of the undissociated acid HX. Table 5 shows that the proton flux, calculated from the $I(t)$ relation, increases after an H^+ gradient has been established with the aid of acids having a high pK value (in the series $HClO_4$, HCl, and HNO_3, the pK are respectively –8, –7, and –1.62 [81]). This fact permits the conclusion that protons are transported in an acid medium in the form of the undissociated acid HX; this has been confirmed by the absence of an effect on j_{H^+} of the surface charge of the membrane, varied by adding the negatively charged phosphatidic acid or the positively charged 3-cetyl(methyl)ammonium bromide, while the addition of cholesterol diminishes j_{H^+} significantly. It is noteworthy that, according to the data of Nichols and Deamer,[90] approximately the same changes in the surface charge of the PC membrane of liposomes led to a significant alteration of the overall permeability coefficient of the membrane for protons and hydroxide ions (by a factor of 3—4). The conclusion that protons are transported through PC membranes of liposomes in the region of pH ~ 3 in the form of the undissociated acid did in fact make it possible to calculate the permeability coefficients P_{HX} for HCl, $HClO_4$, and HNO_3 (only the upper limit was estimated for H_2SO_4) (Table 5). The values of P_{HCl} and P_{HNO_3} obtained by the EPR method are close to those measured[92] on planar lipid membranes ($P_{HCl} \simeq$ 3 cm s^{-1}, $P_{HNO_3} \simeq 10^{-3}$ cm s^{-1}); proton transport through the membrane was also not recorded[92] for H_2SO_4.

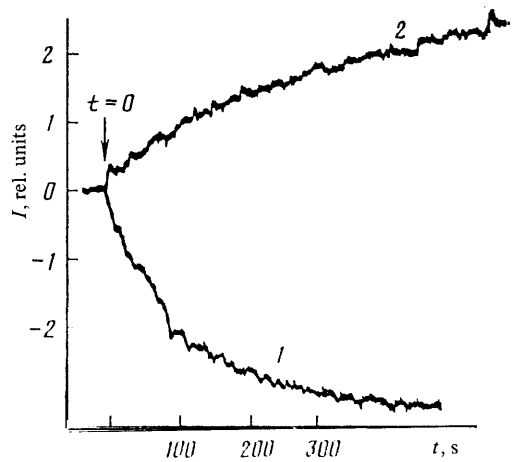


Figure 5. Time variation of the amplitude of the EPR spectrum of the R-Glut radical at the frequency $\omega(pK)$ after the establishment of a transmembrane HCl gradient:[63] 1) pH outside liposomes pH_{out} = 1.63, pH_{in} = 3.13; 2) pH_{out} = 4.63, pH_{in} = 3.13.

A new method for the investigation of the kinetics of proton transport through biomembranes, proposed in a number of studies,[63,86,87] can be extended to the region of neutral and alkaline

pH, since spin probes pH-sensitive in the given regions are now known.

Table 5. Proton fluxes j_{H^+} through the membrane of PC liposomes immediately after the establishment of a transmembrane pH gradient (pH_{out} = 1.63; pH_{in} = 3.13) using various acids and the permeability coefficients P_{HX} of the membrane for these acids.[63,86,87]

Acid	$HClO_4$	HCl	HNO_3	H_2SO_4
j_{H^+}, mol cm litre^{-1} s^{-1}	$2\cdot10^{-10}$	$1.8\cdot10^{-9}$	$3\cdot10^{-8}$	$\lesssim10^{-12}$
P_{HX}, cm s^{-1}	2.2 ± 1	2 ± 1	$(1.4\pm0.7)\cdot10^{-4}$	$\lesssim10^{-7}$

- - -o 0 o- - -

As can be seen from the above discussion, the use of stable NR sensitive to pH makes it possible to obtain quantitative information about the thermodynamic and kinetic characteristics of the very simple proton transfer reaction. Major advances in the organic chemistry of stable radicals[18,101,102] have led to the possibility of a detailed investigation of the influence of steric factors, electron-donating and electron-accepting substituents, and the solvents on the characteristics of the proton transport. Unique experimental possibilities for the study of isotope effects have been created by the application of the EPR method in such systems, including systems in non-aqueous solvents in the absence of solvation effects.

The use of pH-sensitive NR as pH probes in chemical and biological systems is extremely promising. The possibility of introducing hydrophobic and hydrophilic groups into the NR permits their use for the determination of pH within microheterogeneous regions. The determination of pH within cells and certain cell structures, for example, liposomes, is of special interest. Measurement of the rate of proton transport through natural membranes by EPR may prove useful in the solution of many problems in bioenergetics.

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NMR Spectroscopy of Polyfluorinated Allyl Cations

V.I.Bakhmutov and M.V.Galakhov

The results of the NMR study of the hydrocarbon allyl cations are briefly surveyed. The ^{13}C and ^{19}F NMR spectra of polyfluorinated cyclic and acyclic allyl cations are considered and the spectral features of their formation in solutions are discussed. The influence of substituents and of the positive charge on the chemical shifts and the spin-spin coupling constants $^1J(^{13}C-^{19}F)$ and $^4J(^{19}F-^{19}F)$ of polyfluorinated allyl cations are considered. NMR data are presented on the relative stabilities of polyfluorinated allyl cations.
The bibliography includes 85 references.

CONTENTS

I. Introduction 839
II. NMR spectra and charge distribution in hydrocarbon allyl cations 840
III. ^{13}C and ^{19}F NMR spectroscopy of polyfluorinated allyl cations 843

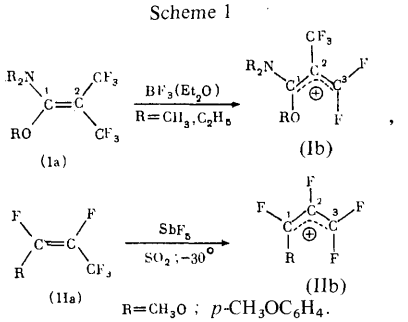
I. INTRODUCTION

The study of the structures, thermodynamic stabilities, and reactivities of carbenium ions remains one of the most rapidly developing fields in modern organic chemistry of current interest. Since the publication of the first studies by Olah (see, for example, Ref.1), already regarded as classical, which have laid the foundations of this field and have made an appreciable contribution to its development, an enormous amount of data has accumulated in the world literature on carbonium ions with the most varied structures and on their properties, spectroscopic characteristics, and reactivities.[2] The ^1H and ^{13}C NMR spectroscopy has played a decisive role in the establishment and development of the chemistry of carbenium ions. The results obtained by this method have in essence led to the formulation of new fundamental concepts in the theory of the chemical bond. On the other hand, the experimental difficulties in the detection and investigation of charged organic species have exerted a certain influence on the improvement of the NMR experimental technique and on the search for increasingly new features relating the spectroscopic and structural characteristics of organic molecules.[3,4]

Studies on cations of the allyl type have made a major contribution to the formulation of the fundamental ideas in the chemistry of carbenium ions. The ^1H NMR spectra of allyl and 2-methylallyl cations, published in 1964,[5] induced an avalanche-like development of this field, which is indicated by hundreds of publications devoted to the investigation of the structures of positively charged allyl system (see, for example, Refs.6-11). However, until very recently there was virtually no information in the world literature about the polyfluorinated allyl cations, which have been merely postulated as intermediate species in electrophilic alkenylation reactions of fluoroolefins in the presence of Lewis acids.[12-14]

The theoretical interest in polyfluorinated allyl cations can be accounted for also by the following factors. The direct observation of α-fluoro-αα-diphenyl- and αα-difluoro-α-phenyl-methyl cations by ^{19}F NMR[8,11] has made it possible to put forward the concept of the ability of the fluorene atom to stabilise the positive charge localised on a neighbouring carbon atom. However, this concept, which has been convincingly justified experimentally in relation to cations of the alkyl type, for a long time clearly conflicted with the unsuccessful attempts to obtain perfluorinated allyl cations by treating perfluoropropene[8,14] and perfluorocyclobutene[14,15] with antimony pentafluoride. The perchlorinated allyl cation has been isolated in the form of the solid salt $C_3Cl_5AlCl_4$,[16] which in fact suggested that fluorine exerts an influence which is the opposite of that of chlorine, namely a destabilising influence in the case of allyl systems.[17] At the same time, the introduction of markedly electron-donating groups in the 1-position in perfluoroisobutene and perfluoropropene makes it possible to obtain smoothly the corresponding cations:[14,18]

Scheme 1



(Ib) (IIb)

The present review, which is based on the literature of the last five years, is in fact devoted to the resolution of the uncertainties which have thus arisen.

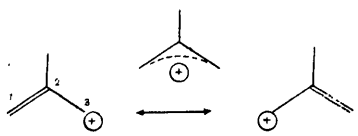
The main method for the investigation of carbonium ions and carbanions is known to be NMR spectroscopy, which makes it possible not only to detect the appearance of a charged centre in the molecule but also to investigate in detail the structural features of the species formed. This is based on the comparatively simple relations found at the present time between the spectroscopic and structural parameters of organic molecules.[3,4] On the other hand, in the case of the ^{19}F and ^{13}C NMR of organofluorine compounds,[19,20] the problem of spectroscopic-structural relations is still far from being resolved. The present review therefore also has a methodological purpose—to survey the characteristic features of the NMR spectra of polyfluorinated allyl cations.

II. NMR SPECTRA AND CHARGE DISTRIBUTION IN HYDROCARBON ALLYL CATIONS

Before discussing polyfluorinated allyl cations, it is useful to consider briefly data on the hydrocarbon allyl cations, demonstrating the possibilities of NMR spectroscopy in the study of the structures of such species in solutions.

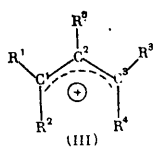
According to the current classification,[11] allyl cations can be regarded as cations of the classical type with the localisation of the positive charge on the terminal carbon atoms,[21,22] as shown in Scheme 2, from which the difference between the terminal and central atoms evidently follows:

Scheme 2



Accordingly, the analysis of the ^{13}C NMR spectra of a large number of acyclic cations having the general formula (III), presented in Scheme 3,[23,24,26–28] shows that the transition from the precursors (olefins) to cations is accompanied by appreciable downfield shifts (up to 100 p.p.m.) of the ^{13}C signals in the 1- and 3- positions so that the C(1, 3) chemical shifts δ are always significantly greater than the shifts δ for the C(2) nuclei in the same cation:

Scheme 3



(III)

R^{1-5}=H [5]; R^{1-4}=H, R^5=CH_3 [5];
$R^{1,3,5}$ = H, $R^{2,4}$ = CH_3 [23, 24]; $R^{1,3,5}$ = CH_3, $R^{2,4}$ = H [24]
$R^{1,3,5}$ = H, $R^{2,4}$ = cyclopropyl [23]
$R^{1,2}$ = CH_3, R^{3-5} = H [23]; R^{1-3} = CH_3, $R^{4,5}$ = H [27]
$R^{1,3}$ = Ph, $R^{2,4,5}$ = H [23]
R^{1-4} = CH_3, R^5 = H [24]; R^{1-5} = CH_3 [24]
R^{1-3} = CH_3, $R^{2,4}$ = H, R^5 = Ph [24]
$R^{1,2}$ = CH_3, $R^{4,5}$ = H, R^3 = CH=C $(CH_3)_2$ [25]
R^1 = CH_3, R^{2-5} = H [26]; $R^{1,2,5}$ = CH_3, $R^{3,4}$ = H [27]
$R^{1-3,5}$ = CH_3, R^4 = H [27]

[Here and henceforth the numerals in square brackets denote references (Translator)].

Thus the relative positions of the C(1 – 3) signals in the ^{13}C NMR spectra correspond satisfactorily to the structure of the allyl cation, agree with the *ab initio* calculations of the π-electron density on the atoms of the allyl triad, and hence can be used successfully for the identification of systems of this kind in solutions. As regards the ^1H NMR spectra, in this case there is no unambiguous correspondence with the charge distribution scheme (Scheme 2).[5,25] Indeed, despite the fact that, on passing from the precursors to the cations downfield shifts of the signals are indeed observed in the ^1H NMR spectrum, there are nevertheless by no means infrequent cases where $\delta(^1H)$ for C(2) is greater than for the C(1, 3) atoms bearing a positive charge. This effect has been observed for example, for the simplest allyl cation (II) with R^{1-5} = H where $\delta(^1H)$ for C(2) is 9.64 p.p.m., whereas $\delta(^1H)$ for the terminal carbon atoms are smaller (δ = 9.0 p.p.m.).[5] Fig.1 indicates the ranges of the $\delta(^1H)$ and $\delta(^{13}C)$ for allyl cations (Scheme 3) which partly illustrates what has been said above.

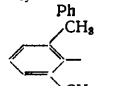
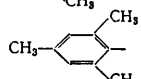
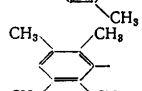
The change in the nature of the substituents in allyl cations naturally leads to a redistribution of their charge density, which is also reflected in the ^{13}C NMR spectra. Thus the successive introduction of methyl groups into the allyl cation (III) has a significant influence on the positions of the signals in the ^{13}C NMR spectra in such a way that a linear relation is observed between the observed values of $\delta(^{13}C)$ and the π-charge density calculated by the *ab initio* method:[22]

$$\delta^{13}C = (433 \pm 11) - (449.5 \pm 22.2)\, q^{\pi},\ r = 0.97 \qquad (1)$$

Relations of this kind make it possible to investigate the distribution of charge density in the allyl cations[23] presented in Table 1. Evidently the shifts δ for the terminal carbon atoms are comparatively close in the case of the 1,3-disubstituted cations. On the other hand, for the 1,1-disubstituted allyl cations the difference δ[C(1)] – δ[C(3)] is large and can reach 120 p.p.m., which in fact permits the conclusion that there is a non-uniform charge distribution between the 1- and 3-atoms, namely that the charge is localised predominantly at C(1). The degree of charge localisation is then determined by the nature of the substituent and, on the basis of the values of $\delta[^{13}C(3)]$, decreases in the following sequence: cyclopropyl ≳ Ph > CH_3.[23] Indeed, in this series $\delta[^{13}C(3)]$ increases by 25 p.p.m. [we may note that in situations of this kind it is correct to compare the values of δ not for C(1) but for C(3) to which the substituent being varied is linked directly].

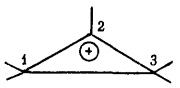
Table 1. The ^{13}C chemical shift of the allyl cations.

$R^1R^2C^1 \overset{2}{=\!=} CH \overset{3}{=\!=} CHR^3$ (⊕)

R^1	R^2	R^3	δ(^{13}C), p.p.m. C(1) C(2) C(3)	Refs.
cyclo-Pr	H	CH_3	227.0 139.4 194.7	[23]
Ph	H	CH_3	196.9 136.5 205.1	[23]
	H	CH_3	199.9 138.1 188.9	[28]
	H	CH_3	193.2 137.1 184.8	[28]
	H	CH_3	197.5 139.5 189.8	[28]
cyclo-Pr	H	Ph	218.1 132.0 181.2	[23]
cyclo-Pr	CH_3	H	249.6 141.8 150.3	[23]
cyclo-Pr	cyclo-Pr	H	276.4 132.7 148.5	[23]
Ph	Ph	H	227.0 136.2 149.5	[23]
cyclo-Pr	Ph	H	234.6 133.8 157.7	[23]

The principal mechanism of the stabilisation of the positive charge in acyclic allyl cation is *p*, π conjugation, which leads to the localisation of the charge on the ends of the allyl triad. However, when the distance between the terminal carbon atoms is shortened, direct overlap of their orbitals with increase in the resonance contribution of the structure (IV), ensuring the appearance of a positive charge on the central carbon atom (the so called 1,3-interaction[29]), becomes

possible in principle.



(IV)

From the standpoint of NMR, this method of charge stabilisation, together with the classical method, should correspond to the equalisation of the values of δ[C(1−3)] and δ(H) for the given atoms.

For this reason, 1,3-interaction as a method of charge stabilisation was initially invoked to account for the similarity of the values of $\delta(^1H)$ and δ[C(1−3)] for the simplest allyl cation,[5] which, however, was not confirmed by quantum-chemical calculations.[30] On the basis of purely geometrical considerations, 1,3-interaction may be expected for the four-membered cyclic cations (V) (Scheme 4), exhaustive information about which has been published.[31,32] Some of these data are presented in Table 2, from which it follows that a shift of the ^{13}C and ^1H signals of the C(2)−H fragment an even weaker field, compared with the signals of the C(1, 3)−H fragment,

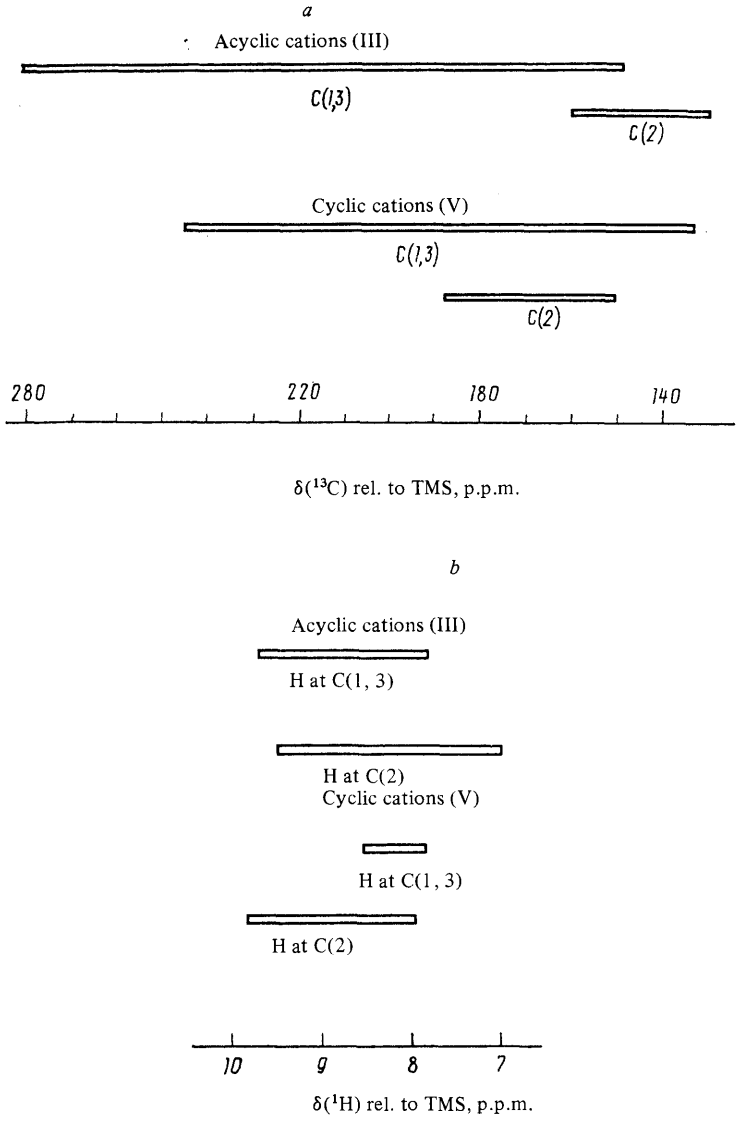
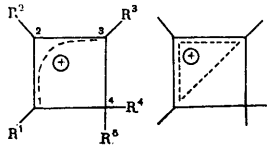


Figure 1. The scales of the ^{13}C (a) and ^1H (b) chemical shifts of hydrocarbon allyl cations.

is characteristic of the compounds considered, with the exception of the last.

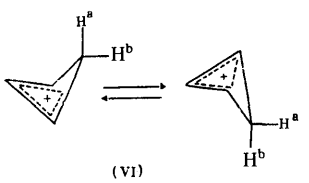
Scheme 4



(V)

$R^{1-5} = H$; $R^{1-4} = H$, $R^5 = Cl$; $R^{1-4} = H$, $R^5 = F$; $R^{2,4,5} = H$, $R^{1,3} = CH_3$;
$R^{1-4} = CH_3$, $R^5 = H$; $R^{1-4} = CH_3$, $R^5 = Cl$; $R^{1-4} = CH_3$, $R^5 = F$;
$R^{1,4} = H$, $R^{2,3} = CH_3$, $R^5 = Cl$; $R^{1,4} = H$, $R^{2,3} = CH_3$, $R^5 = F$;
$R^{1,3} = Ph$, $R^{2,4,5} = H$; $R^{1,3} = Ph$, $R^{2,4} = CH_3$, $R^5 = H$;
$R^{1-4} = Ph$, $R^5 = H$; $R^{1-4} = Ph$, $R^5 = Br$; $R^{1,4,5} = F$, $R^{2,3} = Ph$.

Thus NMR data for the first three cations suggest a distribution of their positive charge throughout the allyl system, as shown in Scheme 4. On the other hand, the introduction of methyl groups into the 1- and 3-positions in the cyclobutenyl cations alters the situation and, as can be seen from Table 2, shifts the C(1, 3) and C(2) resonance downfield and upfield respectively, thus making their spectral parameters closer to the parameters of acyclic allyl cations (Table 1). Consequently, according to NMR data, the probability of the 1,3-overlap depends on the nature of the substituents in the 1- and 3-positions and diminishes with increase in their ability to stabilise the positive charge on the α-carbon atom. Indeed, substituents such as Ph and F exhibit an analogous "spectral" activity.[31,32] Here it is essential to note that all the considerations put forward by the above workers[31,32] and described above are based on a "chemical shift–atomic charge" relation of type (I), which holds in the series of cations considered. However, the chemical shifts of the ^{13}C nucleus occupying the α-position relative to the carbon atom with sp^2 hybridisation in four-membered rings are known to be anomalously high;[33] this is due to the unique nature of the structural and orbital properties of the four-membered ring, which leads to an additional increase in the paramagnetic component of the ^{13}C shielding constant. In other words, the similarity of the values of δ for the C(1, 2, 3) nuclei or the observation of the C(2) signal in an even weaker field than for the C(1, 3) signals may be induced also by this cause and not by the uniqueness of the distribution of charge density. However, the magnetic non-equivalence of the H^a and H^b protons of the cyclobutenyl cation (VI), which is manifested in the NMR spectrum at a low temperature[31] and indicates a non-planar structure of the ring, suggests that the above conclusions[31,32] are correct.

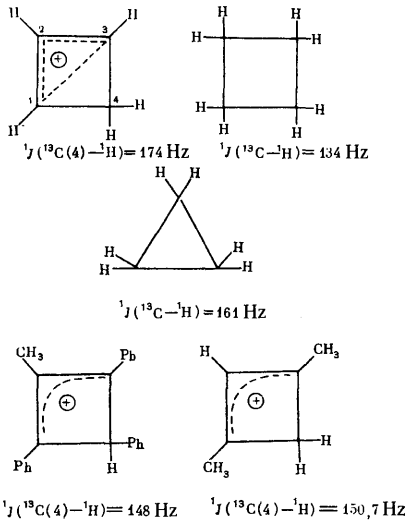


(VI)

This is also indicated by the study of the dependence of $\delta(^{13}C)$ for the allyl triad in cyclic cations on the ring size,[35] which has shown that the 1,3-interaction is pronounced only in the cyclobutenyl cation and is not manifested in the ^{13}C NMR spectra of five- and six-membered structures.

In discussing the question of the 1,3-interaction, it is of interest to consider how such overlap is reflected in the spin–spin coupling constants $J(^{13}C-{}^{1}H)$, which in the case of cycloalkanes are extremely sensitive to angular deformations and increase with decrease in the ring size.[34] It is known that the constants $^{1}J(^{13}C-{}^{1}H)$ increase when a positive charge appears on the carbon atom, the increase being mainly due to the Fermi-contact contribution.[4] We shall therefore consider the values of the direct constants $J(^{13}C-{}^{1}H)$ characterising the unchanged carbon atom in the 4-position in cyclobutenyl cations and carrying information about the geometrical structure of the ring. As can be seen from Scheme 5, $^{1}J[^{13}C(4)-{}^{1}H]$ = 174 Hz for the cyclobutenyl cation and exceeds greatly the analogous constant for cyclobutane and only slightly that for cyclopropane (Scheme 5).

Scheme 5



On the other hand, the substitution of the hydrogen atoms in the 1- and 3-positions by methyl and phenyl groups increases the direct constants $J[^{13}C(4)-{}^{1}H]$, which corresponds to a decrease in the degree of 1,3-interaction.

Table 2. The ^{1}H and ^{13}C chemical shifts of substituted cyclobuteyl cations (V).[31,32]

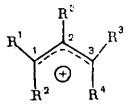
R^1	R^2	R^3	R^4	R^5	δ(^{1}H), p.p.m.				δ(^{13}C), p.p.m.			
					H (1)	H (2)	H (3)	H (4)	C (1)	C (2)	C (3)	C (4)
H	H	H	H	H	7.95	9.72	7.95	4.53	133.5	187.6	133.5	54.0
H	H	H	Cl	H	8.38	9.80	8.38	6.62	141.6	176.7	141.6	63.7
H	H	H	F	H	8.58	9.90	8.58	6.92	136.7	173.8	136.7	86.8
CH_3	H	CH_3	H	H	2.93	8.03	2.93	3.90	197.6	163.1	197.6	51.4

Thus, in conclusion of this Section of the review, one may state that NMR spectroscopy (and in the first place ^{13}C NMR) makes it possible to obtain unique and reliable information about the structure of allyl cations in solutions.

III. ^{13}C AND ^{19}F NMR SPECTROSCOPY OF POLYFLUORINATED ALLYL CATIONS

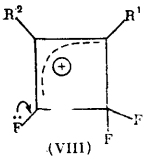
As stated above, the first attempts to obtain polyfluorinated allyl cations by treating perfluoropropene and perfluorocyclobutene with SbF_5 in SO_2 and SO_2FCl were unsuccessful[8,14,15] despite the fact that certain fluorinated cyclic and acyclic allyl cations containing electron-donating groups in the 1-position had been obtained under similar conditions and characterised by ^{19}F NMR.[13,15,18,36] However, in recent years the appliation of this methodological procedure (treatment of fluoro-olefins with SbF_5 in SO_2FCl or in the SbF_5 bulk phase) permitted the synthesis of a whole series of polyfluorinated allyl cations, including the perfluoroallyl and perfluoromethylallyl cations (the references are given in Scheme 6). Some of them proved to be stable and long-lived species even at room temperature. The negative results of the studies quoted above[8,14,15] are therefore incomprehensible. This is presumably due to the inadequate degree of purification of SbF_5 and SO_2FCl.

Scheme 6



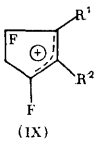
(VII)

$R^1 = Alk_2N$, $R^2 = AlkO$, $R^{3,4} = F$, $R^5 = CF_3$ [18];
$R^1 = n\text{-}CH_3OC_6H_4$, $R^{2-5} = F$ [14]; $R^{1,2,5} = Cl$, $R^{3,4} = F$ [37];
$R^{1,2} = Cl$, $R^{3,4} = F$, $R^5 = CF_3$ [37];
$R^{1,2,5} = Cl$, $R^3 = F$, $R^4 = C_2F_5$ [37]; $R^{1-4} = F$, $R^5 = CF_3$ [38];
$R^{1-4} = F$, $R^5 = H$, Cl,Br, F [39];
$R^{1,3,4} = F$, $R^5 = CF_3$, $R^2 = I$, Br, Cl, OCH_3 [40];
$R^{1,2,4,5} = F$, $R^5 = CF{=}CF_2$ [41]; $R^{1-3,5} = F$, $R^4 = H$, Cl, Br .

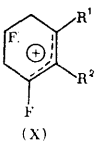


(VIII)

$R^1 = OCH_3$, $R^2 = F$, Cl, OCH_3, SCH_3 [15, 36];
$R^1 = OCH_3$, $R^2 = C_2F_5$, F, OCH_3 [42].



(IX)



(X)

$R^1 = OCH_3$, $R^2 = CF_3$ [42] $R^1 = OCH_3$, $R^2 = C_2F_5$ [42] .

Scheme 6 presents the polyfluorinated allyl cations known at the present time and Fig.2 indicates the $\delta(^{13}C)$ and $\delta(^{19}F)$ scales characterising these species. Analysis of the spectral chraracteristics of the acyclic cations (VII) permits the following generalisations. On passing from the precursor fluoro-olefin to allyl cations, downfield shifts of the C(1) signals ($\Delta\delta$ = 20–80 p.p.m.) and C(3) signals ($\Delta\delta$ = 50–65 p.p.m.) are recorded in the ^{13}C NMR spectra with the virtual retention of the position of the C(2) signal (small changes in δ for this signal, both downfield and upfield, are observed as a function of the nature of the olefin and the cation), which indicates the localisation of the charge on the terminal fragments of the allyl system. This is also demonstrated by the very fact of the observation of the C(1, 3) signals in a weaker field than the C(2) signal (Fig.2). Analogous effects are characteristic also of the ^{19}F NMR spectra. The ^{19}F NMR spectra of the cations illustrated in Scheme 1 are an exception. For example, on passing from the olefins (IIa) to the corresponding cations (IIb), extremely small downfield shifts

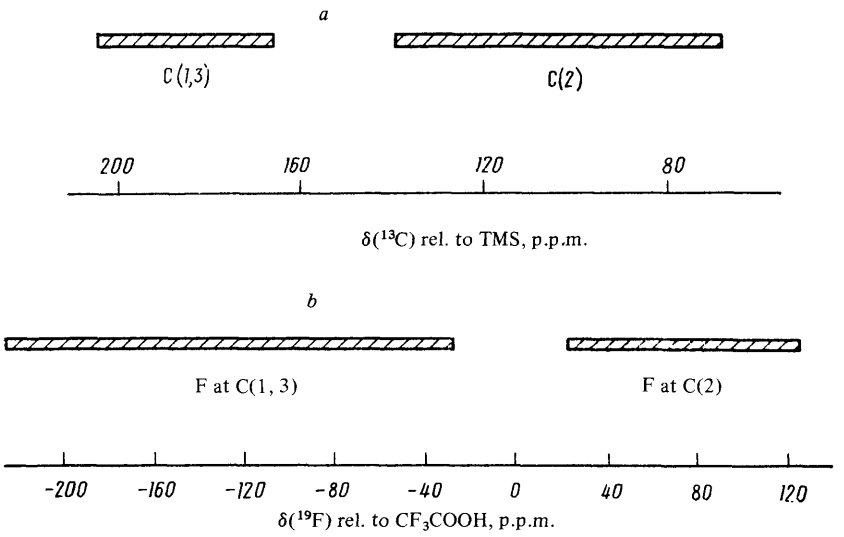
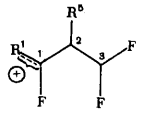


Figure 2. The scales of the ^{13}C (a) and ^{19}F (b) chemical shifts of polyfluorinated allyl cations.

are characteristic of the ^{19}F nuclei in the 3-position, while the downfield shift of the signal of the ^{19}F nuclei at C(1) is by more than 90 p.p.m., which corresponds to the localisation of the charge on the C(1) atom in the structure (XI).[14]



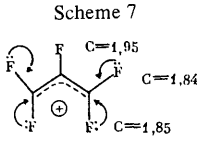
(XI)

$R^1 = p\text{-}CH_3OC_6H_4$
$R^5 = F$,
$R^1 = CH_3O$, $R^5 = CF_3$

An analogous conclusion that the positive charge is localised preferentially in the 1-position has been reached for the cation (VII), with $R^{1,3,4} = F$, $R^5 = CF_3$, and $R^1 = OCH_3$, on the basis of ^{19}F and ^{13}C NMR data.[40] In this case, on passing from the precursor to the cation, a downfield shift of the signal due to the OCH_3 group ($\Delta\delta$ = 15 p.p.m.) is observed in the ^{13}C NMR spectrum. Furthermore, this cation is characterised by a rapid rotation about the C(1)=C(2) bond, which can be retarded only at -70 °C on the ^{19}F NMR time scale (188.3 MHz).

Examination of the generalised spectral parameters presented in Figs.1 and 2 permits the conclusion that in the case of polyfluorinated allyl cations the signals of the C(1) and C(3) atoms, carrying a positive charge, are recorded in a weaker field compared with their hydrocarbon and chlorine-containing analogues.[37,39] On the other hand, the signals of the ^{19}F nuclei at the C(1, 3) atoms in fluorinated allyl cations are observed in extremely weak fields and their chemical shifts reach values down to -200 p.p.m. relative to CF_3COOH. These features of the NMR spectra of the cations (VII) have been explained by the involvement of the fluorine atoms in the delocalisation of the positive charge via the reverse suply of the *p*-electron density (Scheme 7) which has been confirmed by calculations of the charge distribution by the INDO[43] and MNDO[41,44] methods.

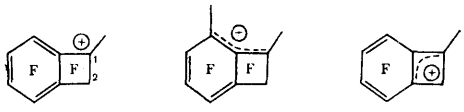
Scheme 7



We may note that, according to the *ab initio* calculation, the introduction of a fluorine atom in the 1-position in the simplest allyl cation increases its stability by 2.8 kcal mol^{-1}.[45]

Virtually analogous changes in the ^{19}F and ^{13}C NMR spectra have been observed on passing from the initial cyclic olefins to the corresponding cations (VIII)–(X).[15,36,42] In describing the delocalisation of the positive charge in the cyclobutenyl cation (VIII) with $R^1 = OCH_3$ and $R^2 = F$,[15] 1,3-interaction was postulated on the basis of the downfield shift of the signal of the ^{19}F nucleus in the 2-position, observed on passing from the precursor to the cation. However, the study of the ^{13}C NMR spectra of the series of cyclic allyl cations (VIII)–(X), containing four-, five-, and six-membered fragments, did not confirm this hypothesis. It was shown that the C(2) signal for such cations is located at stronger fields compared with the C(1, 3) signals and that the difference between their chemical shifts $\delta[C(1, 3)] - \delta[C(2)]$ is 36–63 p.p.m.[42]

Thus experimental and theoretical data have accumulated in recent years which has made it possible not only to provide a firm answer to the previously controversial question of the existence of polyfluorinated allyl cations as kinetically independent species but also to represent the distribution of their positive charge. Unfortunately, there is as yet no information in the literature about the perfluorocyclobutenyl cation.[14,15] Its only and purely speculative analogue is the perfluorobenzocyclobutenyl cation (XII), which has been detected by ^{19}F NMR[46] and to which the authors have attributed the structure of the carbenium ion (XIIa) on the basis of the large shift of the ^{19}F resonance at C(1), observed on passing from the precursor to the cation ($\Delta\delta$ = 145 p.p.m.).



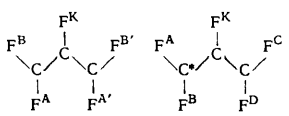
(a) (b)

(XIII)

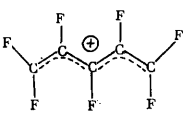
1. Characteristic Features of the ^{19}F and ^{13}C NMR Spectra of Polyfluorinated Acyclic Allyl Cations

The ^{19}F NMR spectra of organofluorine compounds are characterised by high values of *J*, which reach hundreds of Hz units.[19,47] Precisely for this reason, situations frequently arise where the differences between the chemical shifts $\Delta\nu$ become comparable to the spin–spin coupling constants ($J/\Delta\nu \geqslant 0.1$), which leads to the appearance of the NMR spectra of strongly bound spin systems,[48] in which the differences of the absorption frequencies of the spectral lines do not correspond to the real values of *J*. Hence it follows that, in order to obtain the true values of δ and *J* and hence in order to identify the structure, the complete quantum-mechanical calculation of such structures is necessary.[49] We shall explain this in relation to several examples. It has been noted[37] that, after the addition of SbF_5 to perfluoropropene, complex multiplets appear in the ^{19}F NMR spectrum in the -89 – -100 and +117 p.p.m. regions (relative to CF_3COOH), which were later identified[39] as the spectrum of a five-spin system of the type AA'BB'K (Scheme 8), which in fact makes it now possible to make the unambiguous claim that the perfluoroallyl cation is formed in the given mixture.

Scheme 8



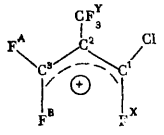
Similarly the agreement between the theoretical spectrum of the seven-spin system, containing more than 140 bands, with the experimental spectrum demonstrates the formation of the perfluoropentadienyl cation which exists in solution in the form of the *s-trans*, *s-trans*-isomer (XIII):



(XII)

This is also confirmed by quantum-chemical calculations by the MNDO method,[41] according to which the *s-trans*, *s-trans*-structure is

energetically more favourable. The ^{19}F NMR spectrum of the *cis-isomer* of the 1-chloro-2-trifluoromethylallyl cation (XIV) is of interest as regards the complexity of the interpretation.



(XIV)

Thus, in the −144 p.p.m. region, it is possible to observe six signals in the above spectrum (Fig.3), each of which is split into a quartet with a non-equidistant disposition of lines. Calculation of the spectrum[40] permitted the classification of the given multiplet as the X-component of the $ABXY_3$ system and made it possible to obtain the true spin−spin coupling constants and hence to identify the cation investigated. Thus the principal feature of the ^{19}F NMR spectra of acyclic fluorinated allyl cations is their complex character. The ^{13}C NMR spectra of these cations are also complex, especially in the case of the symmetrical 2-substituted structures (VII) with R^{1-4} = F.[38,39] We shall illustrate this in relation to the perfluoroallyl cation as an example (Scheme 8). It was stated above that the ^{19}F NMR spectrum of this cation corresponds to the AA'BB'K spin system and is therefore rigorously symmetrical. On the other hand, on passing to ^{13}C NMR, the spectrum loses symmetry and is calculated as the X-component of another spin system, namely ABCDKX (Scheme 8).[39] Such a change in the type of spin system formed by the ^{19}F nuclei, is due to the specific features of the recording of the ^{13}C spectra, namely the isotopic shift on passing from ^{12}C to ^{13}C [50-52] and the associated loss of symmetry by the molecule. The isotopic shift of the signals due to the fluorine nuclei in all the 2-substituted analogues of the perfluoroallyl cation is 0.11 p.p.m.[39] In conclusion, we may note yet again that, despite the by no means simple procedure used to calculate the ^{13}C and ^{19}F NMR spectra of fluorinated allyl cations, requiring a certain amount of time, this approach is absolutely essential both for the establishment of the fact of their formation in solutions and in order to obtain accurate values of their spectral characteristics, including the signs of the constants J, whose knowledge permits the investigation of the relations between the spectral and structural parameters. Some of these relations are described below.

2. The "^{13}C Chemical Shift−Atomic Charge" Relation for Polyfluorinated Allyl Cations and Olefins as an Example

One of the central questions in NMR spectroscopy is the relation between the values of δ and the electron distribution in the molecules. According to Saika and Sliehter,[53] the shielding constants of the magnetically active nucleus can be represented by the sum of three terms [Eqn.(2)]:

$$\sigma=\sigma_d+\sigma_p+\sigma_a \ , \qquad (2)$$

where σ_d is the diamagnetic contribution, σ_p the paramagnetic contribution, and σ_a represeents the sum of the shielding constants due to the magnetic anisotropy of the bond, the influence of the solvent, etc. The ideas concerning the shielding constant of the ^{13}C nuclei[54-56] permit the assumption that in this case the paramagnetic contribution plays a decisive role. It is expressed by the simplified equation[56]

$$\sigma_p=(-e^2h/2m^2c^2\Delta E)\langle r^{-3}\rangle(Q_{AA}+\Sigma Q_{AB}) \ , \qquad (3)$$

where e, h, m, and c are known constants, ΔE is the average excitation energy, r is the distance between the nucleus and the $2p$ electrons, and Q_{AA} and Q_{AB} are elements of the "charge density/bond order" matrix. The first report of the observation of a correlation between the experimental values of $\delta(^{13}C)$ and the charge q' [Eqn.(4)] appeared after the comparison of the ^{13}C NMR spectra of aromatic molecules with the π-charge density calculated by the Hückel

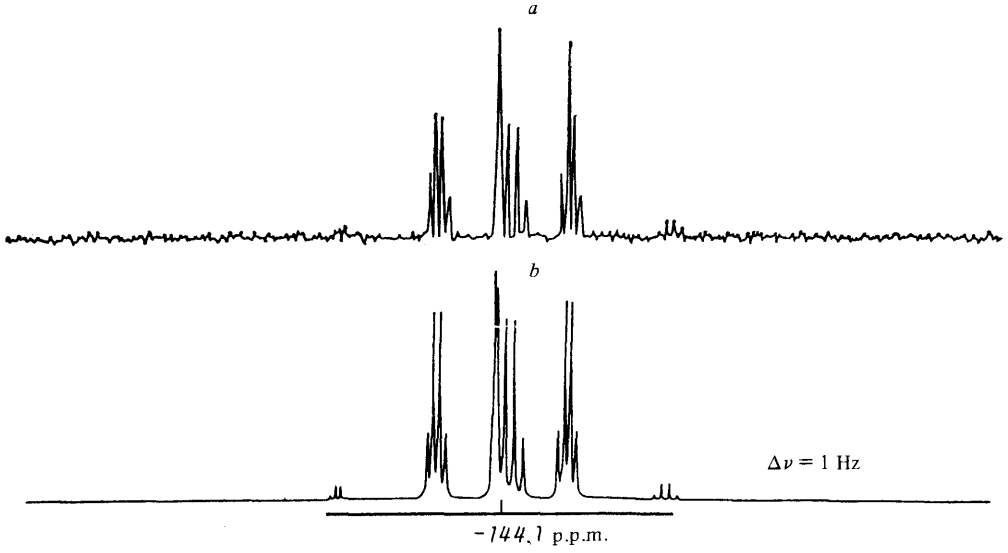


Figure 3. The experimental (a) and theoretical (b) spectra of the X-component of the type $ABXY_3$ spin system of the cation (XIV).[40]

method:[57]

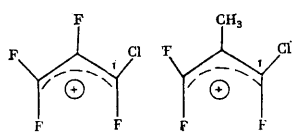
$$\delta^{13}C = A q^t + B$$
$$A = 160 \text{ p.p.m./electron.} \quad (4)$$

The above linear relation can be explained by the fact that the main charge-dependent term in Eqn.(3) is $<r^{-3}>$ (ΔE and Q remain constant on passing from one compound to another); this is confirmed by calculations of the atomic charges and the parameter r for a large number of organic compounds.[58,59] Among studies published later, devoted to the investigation of the "^{13}C chemical shifts – atomic charge" relation (see, for example, Refs.59–63), the study of Baumann and Olsen[59] in which this relation was analysed for 20 organic compounds (50 values of δ), including aromatic cations and anions, is of special interest in our view. The results obtained showed that (1) the coefficient A in Eqn.(4) depends on the LCAO-MO method used for the calculation, (2) that the change in the character of the chemical bond and in geomtetry on passing from one compound to another precludes the description of the "δ(^{13}C) – charge" relation by simple linear equations of the type of Eqn.(4) as a consequence of the change in Eqn.(3) of not only r but also of other parameters, and (3) in the analysis of the relation of the "δ(^{13}C) – charge" type it is essential to take into account also the diamagnetic component of the shielding constant. Summarising the foregoing, one may conclude that it is completely obscure in what way the simplified but nevertheless still complex Eqn.(3) frequently reduces in practice to simple equations of type (4). Nevertheless, this has been established for many classes of organic compounds and it has even been suggested that relations of this type be used for the computer analysis of ^{13}C NMR spectra.[64]

In the study quoted above,[59] a deviation of fluorine-containing compounds from the so called "δ(^{13}C) – charge" correlations was reported. This concerns, for example, δ[C(1)] for the 1-fluorobenzocyclopropyl cation. On the other hand, it has been shown that, on passing from fluorinated olefins to the corresponding allyl cations (VII), downfield shifts of the C(1, 3) resonance are observed in the ^{13}C NMR spectra[38,39] and, conversely, on formation of carbanions from fluorinated cycloalkenes, upfield shifts, reaching 70 p.p.m., are characteristic of the carbon atom carrying the negative charge.[65] Thus there are grounds for seeking correlations of type (IV) also in the case of organofluorine compounds. The geometries and charge density distributions in polyfluorinated olefins and acyclic allyl cations have been calculated[41,44,66] by the LCAO-MO MNDO method. This made it possible to analyse[67] 27 values of δ(^{13}C) as a function of the overall atomic charge of the sp^2-hybridised carbon atom q^t and to observe the linear relation

$$\delta_{^{13}C} = (84.2 \pm 7.5) q^t + (124.4 \pm 3.8), \; r = 0.93 \; , \quad (5)$$

which can be used to estimate the atomic charges from ^{13}C NMR spectra. The values of δ for the ^{13}C(1) nuclei in the cations (XV), i.e. for the atoms which are linked directly to the substituent, in the given instance to the Cl atom, deviate from the given correlation to the greatest extent.



cis-, trans- *cis-, trans-*

(XV)

Indeed, on passing from perfluorinated analogues to the cations (XV), the positive charge on the G(1) atom fails as a consequence of the polarisation of the C–Cl bond along the σ-skeleton,[44] while δ(^{13}C) increases significantly (by 20 p.p.m.). Such increase in δ[C(1)] on substitution of fluorine by a "heavy" halogen is in general characteristic of 1-halogeno-derivatives of the perfluoroallyl and perfluoromethylallyl cations (Table 3), the effect being thus opposite in sign to the "heavy" atom effect usually observed in ^{13}C NMR spectroscopy (see, for example, Levy and Nelson[4]), which is illustrated here in relation to fluoro-olefins in Table 3. In order to elucidate the cause of the deviation of the δ(^{13}C) for the C(1) atoms in compound (XV) from the relation (5), the diamagnetic contributions to the shielding constant were estimated[67] by the method of Flygar and Goodisman[69] and then, after introducing the diamagnetic correction ($\delta^{exp} - \delta^d = \delta^p$), the values obtained were again compared with the overall charge q^t. It was found that the application of this correction improves the situation, but again with the exception of the δ[C(1)] points for the cation (XV). Thus one can only assume that, on passing to 1-halogeno-substituted polyfluorinated allyl cations, δ[C(1)] is determined not so much by the change in the charge (or in other words in the parameter $<r^{-3}>$) as by the change in the orbital properties of the C(1) atom replaced by the halogen atom.[67]

Table 3. The ^{13}C chemical shifts of the C(1) atoms of allyl cations and their precursors (p.p.m. relative to TMS_{ext}).

$F_2\overset{3}{C}\overset{2}{=}\overset{1}{C(X)}\overset{+}{\cdots}CFY$; $\overset{3}{CF_3}-\overset{2}{C(X)}=\overset{1}{C}FY$

Cation		δ(^{13}C)	Olefin		δ(^{13}C)	Refs.
X	Y		X	Y		
F	F	170.2	F	F	153.2	[39]
F	Cl*	187.6; 191.0	F	Cl*	140.8; 142.5	[68]
F	Br*	187.6; 193.4	F	Br*	130.3; 133.7	[68]
CF_3	F	176.1	CF_3	F	157.0	[38]
CF_3	Cl*	202.2; 201.0	CF_3	Cl	159.6	[40]
CF_3	Br*	205.0; 202.7	CF_3	Br	150.0	[40]
CF_3	I*	197.5; 194.6	CF_3	I	121.6	[40]
CF_3	Cl**	214.3				[37]

*The two values are quoted for the *cis-* and *trans-*isomers respectively.

**The 1-dichloroperfluoromethylallyl cation.

3. The ^{19}F – ^{19}F Spin – Spin Coupling Constants of Polyfluorinated Allyl Cations

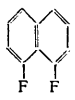
The spin – spin coupling constants play a major role in the determination of the structures of organic compounds and in the study of their electronic structures by NMR.[3] For this reason, it is legitimate to analyse the constants $J(^{19}F - ^{19}F)$ for polyfluorinated allyl cations in order to discover to what extent they are characteristic of the given class of compounds. It follows from the analysis of the ^{19}F NMR spectra[14,18,37–41,68] that the geminal $J(^{19}F - ^{19}F)$ constant (J^{gem}) increases sharply on passing from fluorinated olefins (10–60 Hz) to the corresponding cations (VII) (160–245 Hz), which can be used as the spectroscopic sign of the formation of the given cations. We may note that the constants J^{gem} for allyl cations and fluoroalkanes have similar values. This may be caused by the fact that the F–C(1, 3)–F angle in acyclic fluoroallyl cations is close to the tetrahedral angle and, according to a MNDO calculation carried out with complete optimisation of the geometry, amounts to

110–112°.[41,44] In contrast to the constants J^{gem}, the vicinal (spanning three bonds) $J(^{19}F-^{19}F)$ constants of polyfluorinated allyl cations are not characteristic. Indeed, they are approximately equal for the initial olefins ($^3J^{cis}$ = 6–40 Hz, $^3J^{trans}$ = 117–143 Hz) and for the acyclic cations (VII) ($^3J^{cis}$ = 8–30 Hz, $^3J^{trans}$ = 90 to 124 Hz).

Table 4. The constants $^4J(^{19}F-^{19}F)$ for the allyl cations (VII) (Scheme 6) ($R^1 = R^2 = R^4 = F$[73]).

R^3	R^5	J, Hz				r, Å
		«U»	«W»	«S»	J^{np}	
H	F	−122.4	−92.4	−22.2	−100.2	2.975
F	F	−140.3	−104.5	−30.9	−109.4	2.907
OCH_3	F	−157.6	−101.3	−35.6	−122.0	2.860
Cl	F	−149.6	−92.0	−29.3	−120.3	2.850
Br	F	−150.7	−87.7	−29.4	−121.3	2.821
F	Br	−156.0	—	−42.0	−114.0	2.821
CF_3	F	−146.7	−83.8	−23.2	−123.5	2.775
CF_3	Cl	−175.3	—	−31.5	−143.8	2.644
CF_3	Br	−173.4	—	−36.9	−136.5	2.634

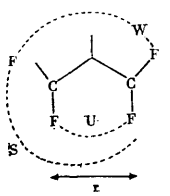
The appearance in the ^{19}F NMR spectra of large long-range (spanning four bonds) spin–spin $^{19}F-^{19}F$ coupling constants (Table 4), which, for the *cis–cis* disposition of the interacting nuclei, exceed by a factor greater than two the ^4J ($^{19}F-^{19}F$) constant for the isostructural but uncharged 1,8-difluoronaphthalene (XVI) fragment, must be regarded as an invariable sign of the formation of fluorinated acyclic allyl cations.[70]



(XVI)

We may note that $J(^{19}F-^{19}F)$ constants spanning six bonds and amounting to 10–12 Hz have been observed for the perfluoropentadienyl cation (XIII).[71] The constants J spanning three and more bonds are known to depend markedly on the mutual orientation of the chemical bonds along the interaction pathway.[19,49,72] Table 4 illustrates this situation for polyfluorinated allyl cations. It follows from the data presented that the constants $^4J(^{10}F-^{19}F)$ decrease in absolute magnitude in the sequence "U" > "W" > "S" (Scheme 9) without change in their sign.[73]

Scheme 9



The deviation from the W-rule, well known for the proton–proton spin–spin coupling constants,[49] can be explained by the spin–spin coupling "through space" in the case of the *cis–cis* orientation. (Examples, mechanisms, and semiempirical theories of the transfer of spin information by-passing chemical bonds can be found in several communications[72,74–80]). Indeed, it has been shown that [73] the "spatial" contribution ($J^{sp} = J^U - J^s$) to $^4J(^{19}F-^{19}F)$ constants for the *cis–cis* orientation (Table 4), which has been differentiated by Bakhmutov et al.,[71] diminishes with increase in the internuclear distant r (Scheme 9) determined by the LCAO-MO MNDO method.[44,73] The experimental dependence is then best fitted, taking into account the sign, by Eqn.(6), whose physical significance can be interpreted in terms of direct overlap of the *p*-electron clouds of the fluorine atoms in close proximity in space:

$$J^{sp} = -431(\pm 50)\exp(-0.16\cdot r^2) + 1.2 \qquad (6)$$

It is noteworthy that the variation of the overlap integral for the fluorine molecule for distances between the atoms exceeding the sum of the van der Waals radii is a function of an analogous type.[73] In the calculation of the constant $J(^1H - ^1H)$ spanning five chemical bonds on the basis of the Fermi-contact mechanism for the *s-cis*-conformation of butadiene, a dependence of $^5J(H-C)$ on the internuclear distance of the Gaussian type was also obtained.[81] Thus, there are grounds for the assumption that the nuclei interacting through space can be regarded as "magnetic probes" for "sensing" the form of the overlapping part of the electron clouds.

4. The $^{13}C-^{19}F$ Spin–Spin Coupling Constants of Polyfluorinated Allyl Cations

The accumulation of extensive data concerning the influence of various factors on the constants for the direct spin–spin coupling (via one chemical bond) with participation of ^{13}C nuclei constitutes the basis of their use for the determination of the structures of organic compounds by NMR.[3] The spectroscopic data on polyfluorinated olefins and allyl cations (VII) permit certain generalisations also for the $^1J(^{13}C-^{19}F)$ constants characterising the sp^2-hybridised carbon atoms and atoms with a hybridisation close to sp^2. A significant (up to 100 Hz) increase in $^1J(^{13}C-^{19}F)$ on passing from fluoro-olefins to the corresponding allyl cations has been noted[37–40,42] (this concerns carbon atoms carrying a positive charge). The constants of the acyclic and cyclic cations (VII)–(X) are themselves in the range from 310 to 410 Hz. We may note that these values greatly exceed the direct $J(^{13}C-^{19}F)$ constants observed in the NMR spectra of related polyfluorinated arenonium ions.[82,83] The foregoing refers to the increase in the spin–spin coupling constants in absolute magnitude, since $^1J(^{13}C-^{19}F)$ is negative.[3,83] More than 30 values of the direct constants $J(^{13}C-^{19}F)$ of fluorinated olefins and allyl cations have been analysed and on this basis it has been established that there is a tendency towards their increase with increase in the positive charge on the sp^2-hybridised carbon atom and with decrease in the negative charge on the neighbouring fluorine atom, which is expressed in the two-parameter correlation[7]

$$^1J(^{13}C-^{19}F) = 92q^C + 501q^F + 325,\ r = 0.89 \qquad (7)$$

However, the one-parameter Eqn.(8), which makes it possible to estimate the atomic charge on the carbon atom using available spectroscopic data, is apparently of greater practical value:

$$^1J(^{13}C-^{19}F) = 122q^C + 277;\quad r = 0.84. \qquad (8)$$

The increase in $^1J(^{13}C-^{19}F)$ following the appearance of a positive charge on C(1, 3) corresponds, in principle, to the increase in the amount of *s* character of the given atom as a result of the splitting off of the fluorine atom from the initial olefin and the subsequent

delocalisation of the *p*-electron density, i.e. is treated within the framework of the Fermi-contact mechanism.[19] However, within the framework of this mechanism, it is difficult to explain the fact that $^1J(^{13}C^1-^{19}F)$ for the cation (XV) is greater than $^1J(^{13}C^3-^{19}F)$ despite the smaller positive charge localised on the C(1) atom (Table 5). Moreover, an increase in the direct constant J with decrease in the electronegativity of the heteroatom of the substituent is characteristic of 1-substituted fluorinated olefins and allyl cations (Table 6). However, in each specific case, the direct $J(^{13}C-^{19}F)$ constant for the cation is significantly greater compared with the olefin. Such complex character of the variation of J under the influence of the substituent and on passing from olefins to cations can apparently be explained by non-concerted changes in the Fermi-contact and spin–orbital contributions,[68] which have been shown by quantum-chemical calculations[83] to be virtually equal for interaction through one chemical bond. Despite this, the constants J discussed should be recognised as characteristic in relation to polyfluorinated allyl cations.

Table 5. The spin–spin coupling constants (SSCC) $^1J(^{13}C-^{19}F)$ and the overall atomic charges (LCAO-MO MNDO) of polyfluorinated allyl cations.[68]

Structure	Isomer	SSCC, Hz	q^C, electronic charge units
$F_2C^3=C^2(F)-CFCl^1$ ⊕	*cis*	−375.9 C (1) −254.0 C (2) −354.7 C (3)	+0.469 −0.047 +0.669
	trans	−375.7 C (1) −274.0 C (2) −357.9 C (3)	+0.455 −0.042 +0.666
$F_2C^3=C^2(CF_3)-CFCl^1$ ⊕	*cis*	−386.2 C (1) −360.7 C (3)	+0.514 +0.716
	trans	−384.0 C (1) −356.2 C (3)	+0.530 +0.724

Table 6. The direct spin–spin coupling constants $^1J(^{13}C-^{19}F)$ for the C(1)–F fragment in the fluoro-olefins $FYC^1=C^2X-CF_3$ and the allyl cations

$$FYC^1-C^2X-CF_2 \quad (\oplus)$$

and the electronegativites E of the substitutent Y.[68]

X	Y	$^1J_{olefin}$, Hz	$^1J_{cation}$, Hz	E
F	F	−272.8	−354.0	4.0
F	H	−291.1*	−364.5*	2.1
F	Cl	−304.0*	−375.9*	3.2
F	Br	−323.0*	−397.5*	3.0
CF_3	F	−306.3	−360.0	4.0
CF_3	OCH_3	−306.7*	−363.2**	3.4
CF_3	Cl	−322.0	−385.1**	3.2
CF_3	Br	−342.6*	−400.4**	3.0
CF_3	I	−351.2*	−408.8**	2.7

*trans-Disposition of F–C–C–X or CF_3–C–C–X.
**Averaged value for the *cis*- and *trans*-isomers.

Information about the values and signs of the constants $^2J(^{13}C-^{19}F)$ and $^3J(^{13}C-^{19}F)$ of polyfluorinated olefins and cations can be found in a number of communications.[37–41] Here we shall note that the values of J spanning three bonds for the *trans*-disposition of the interacting nuclei vary from −9 to −34 Hz. On the other hand, in the case of the *cis*-disposition they change sign and do not exceed 4 Hz in absolute magnitude.

Table 7. Thermodynamic parameters of the formation of polyfluorinated allyl cations.

$$F_2C^3=C^2(X)-CFY^1 \quad (\oplus) \quad [84, 85]$$

X	Y	ΔH, kcal mol^{-1}	ΔS, e.u.	ΔG^{298}, kcal mol^{-1}
F	H	−4.16±0.2	−22.5±0.8	2.6
F	F	−5.6±0.5	−26.1±1.8	1.8
CF_3	F	−4.6±0.1	−23.9±0.8	2.5
CF_3	Br	−6.4±0.8	−28.5±3.0	2.1
CF_3	Cl*	−7.0±0.2	−28.5±0.4	1.5

*The 1,1-dichloroperfluoromethylally cation.

5. ^{19}F NMR Spectra and Relative Stabilities of Polyfluorinated Allyl Cations

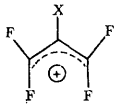
The spectral characteristics of polyfluorinated allyl cations described in the preceding Sections and their characteristic features permit a reliable solution of the problem of the identification of such species in solutions by NMR. Another important problem, namely the problem of the influence of the substituents on the relative stabilities of polyfluorinated allyl cations, can also be solved successfully by NMR. For this purpose, one can use three approaches: (1) the study of the thermodynamics of the equilibrium (9) on the basis of the measurement of the relative integral intensities of the signals of the olefins and cations in ^{19}F NMR spectra at different temperatures:[68,84]

$$CF_3-\underset{R^1}{C}=CFR^2 + SbF_5 \overset{Kp}{\rightleftharpoons} F_2C=\underset{R^1}{C}-CFR^2 \quad (\oplus) + SbF_6^- ; \qquad (9)$$

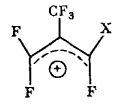
(2) analysis of the ^{19}F NMR spectra of a mixture of two polyfluoro-olefins in the presence of a deficiency of a Lewis acid, i.e. under the conditions of a competing reaction;[85] (3) the study of the kinetic characteristics of the reaction involving the addition of counterions to the corresponding allyl cation[84] on the basis of the analysis of the temperature dependent evolution of the line form in the ^{19}F NMR spectrum containing the olefin and cation signals. The qualitative and quantitative data obtained in this way are compiled in Tables 7

and 8 and in Scheme 10.

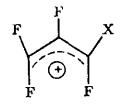
Scheme 10



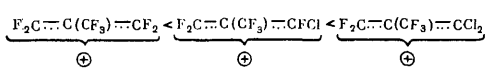
$CF_3 < F < Br < Cl < H$ (a)



$F < Cl < Br < I < OCH_3$ (b)

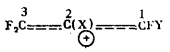


$H < F < Cl < Br$ (c)



As can be seen, the formation of polyfluorinated allyl cations from the corresponding fluoro-olefins in solutions is an energetically favourable process, since the enthalpy of formation ($\Delta H = H^{cat} - H^{ol}$) is always negative. On the other hand, the negative values of ΔS, which are almost identical in all cases, correspond satisfactorily to an increase in order in the system following the appearance of a charge centre in the latter. Comparison of the data in Tables 7 and 8 shows that the kinetically less favourable addition of the counter-ion to the cation corresponds to its high thermodynamic stability.

Table 8. Kinetic parameters of the addition of the fluoride ion to the polyfluorinated allyl cations [84,85]



X	Y	E_a, kcal mol^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	$\Delta G^{298\neq}$, kcal mol^{-1}
F	F	6.2±0.3	6.9±0.3	−8.4±0.4	9.4
Cl	F	21.6±1.3	22.2±1.3	−12.1±1.5	25 5
Br	F	13.7±0.9	14.2±0.9	−15.0±1.0	18.7
CF_3	Cl*	9.5±0.9	8.9±0.9	−16.8±3.2	13.9
Cl	Cl**	11.8±1.1	12.4±1.1	−12.1±2.5	16.0

*The 1,1-dichloroperfluoromethylallyl cation.
**The 1,1,2-trichloroperfluoroallyl cation.

The influence of substituents on the relative stabilities of polyfluorinated allyl cations is expressed by the series presented in Scheme 10. As can be seen, in the case of 2-substituted perfluoroallyl cations (10a) this influence cannot be treated in terms of a change in only the electronic properties of the substituents. It is apparently necessary to invoke also steric factors. The increase in the stability of 1-substituted analogues of the perfluoromethylallyl cation (10b) corresponds to a decrease in the $-I$ effect of the substituent and to an increase in its polarisability. An increase in the number of "heavy" halogens at one of the ends of the allyl system also increases the stability of the given species (10d). The decrease in stability on passing from the perfluoroallyl cation to its 1-hydro-derivative (10c) must be specially emphasised. The observed effect then amounts to 1.5 kcal mol^{-1} (Table 7)[68] and agrees well with the results of a theoretical calculation by the *ab initio* method.[45] It follows from the NMR spectra that the F atom participates in the stabilisation of the positive charge localised on a neighbouring carbon atom via the reverse supply of *p*-electron density. Apparently this ability of the fluorine atom is in fact the cause of the result obtained. Indeed, in the case of the perfluoroallyl cation and its 2-hydro-derivative, i.e. on substitution of the fluorine atom by hydrogen in the 2-position which does not carry a positive charge, the opposite picture (10a) is observed.

---o0o---

The main aim of the present review was to survey the results of the study of polyfluorinated allyl cations which had been regarded for a long time as hypothetical species and had been assumed to exist only as intermediates in electrophilic alkenylation reactions of fluoro-olefins. This uncertainty in the theroretical ideas about the mechanisms of the above reactions and in the chemistry of carbenium ions has now been eliminated as a result of the direct observation by ^{19}F and ^{13}C NMR of a series of polyfluorinated allyl cations (cyclic and acyclic) as both long-lived and kinetically independent species. Presumably data on the stability of allyl cations in solutions and on the distribution of their positive charge will extend the scope of the synthetic use of the reactions in which they are formed as intermediate species.

It may be hoped that the spectral signs of the formation of polyfluorinated allyl cations examined and surveyed in the present review will be of practical use to specialists working in the field of the NMR of organofluorine compounds which is nowadays developing rapidly. Analysis of the literature data devoted to the NMR spectra of fluorine-containing olefins and allyl cations has shown that such compounds can be used successfully as model molecules to establish new relations between spectra and structure.

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Fluoroalkenylphosphonates

A.A.Kadyrov and E.M.Rokhlin

In this review we survey the methods for the preparation of derivatives of fluoroalkenylphosphonic acid and their reactions. The main methods for obtaining these compounds are based on the reactions of fluoroolefins with phosphites and also on the elimination of halogens, hydrogen halides and alkyl halides from fluoroalkylphosphonates or fluorine-containing phosphorus ylides. The chemical properties of fluoroalkenylphosphonates are due to the combined effect of the fluorine atoms and the phosphonate group. Their reactions with different reagents leads to modifications of the phosphonate group, addition to the C=C bond, replacement of the vinyl halogen atom, and cleavage of the C-P bond.
The bibliography includes 96 references.

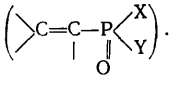
CONTENTS

I. Introduction 852
II. Methods of synthesis 852
III. Chemical properties 857

I. INTRODUCTION

Unsaturated phosphonic acids and their derivatives make up an important class of organophosphorus compounds that are of interest because of the variety of their chemical reactions and their possible practical applications.[1-4] The attention of research workers has in recent years been drawn increasingly towards fluorine-containing alkenylphosphonates. The presence in the same molecule of fluorine atoms, a C=C double bond, and $PO(OR)_2$ groups gives these compounds a unique reactivity, combining the properties of fluoroolefins and unsaturated phosphonates. There are also some examples which confirm the practical value of products derived from them. Some compounds of this type have been proposed as monomers for making cation exchange resins,[5-7] impregnating agents for textiles and paper,[8] intermediates in the synthesis of insecticides and incombustible polymers,[9] extraction agents for heavy metal ions,[10] components of toothpaste[11] and even antibiotics.[12]

The present review attempts to correlate and systematise the information on the methods of obtaining and the chemical properties of fluoroalkenylphosphonic acids and their derivatives, in particular for those compounds in which the phosphonate group is bonded directly to the α-carbon atom of the fluoroalkenyl fragment



In selecting literature data we used the automated formation search system AIPS-FTOR [AISS-FLUORINE] (VINITI) [All Union Institute of Scientific and Technical Information].

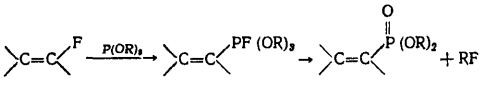
II. METHODS OF SYNTHESIS

Some methods used for obtaining fluoroalkenylphosphonates are essentially no different from those used for their nonfluorinated analogues, in this case being mainly reactions such as dehalogenation and dehydrohalogenation of haloalkylphosphonates. However, specific methods based on the unique reactions of fluoroolefins and other fluorine-containing unsaturated compounds are often used for the synthesis of fluoroalkenylphosphonates.

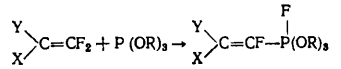
1. Substitution of Vinyl Halogen Atoms in Fluoroolefins

A reaction for "vinyl" substitution of a halogen atom that is typical for fluoroolefins and related compounds is widely used for the synthesis of fluoroalkenylphosphonates containing a C=C bond conjugated with the phosphonate group.

Trialkyl phosphites react fairly readily with polyfluoroolefins to form fluoroalkenylphosphonates:

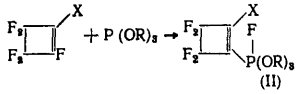


In this case trialkoxyfluorophosphoranes are likely to be formed as intermediates. Phosphoranes such as (I) and (II) are isolated from reactions of trialkyl phosphites with perfluoroisobutylene,[13] polyfluorocyclobutenes,[13,14] perfluoromethacrylates,[15-17] and difluoromethylenemalonates[17,18]†



(I)

R = Et, X = Y = CF_3 (a); R = Me, X = CF_3, Y = COOMe (b), COOEt (c); R = Et, X = CF_3, Y = COOMe (d), COOEt (e); R = Me, X = Y = COOME (f); R = Et, X = Y = COOEt (g)



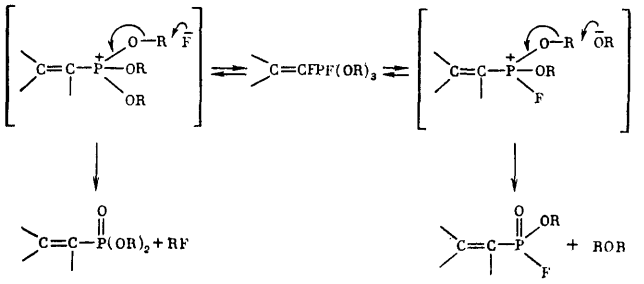
(II)

X = F, R = Me (a), Et (b); R = Me, X = Cl (c), Br (d), I (g)

Thermal decomposition of polyfluoroalkenyltrialkoxyfluorophosphoranes, which may be regarded as intermediates of an Arbuzov rearrangement, usually leads to the formation of alkyl fluorides and dialkyl polyfluoroalkenylphosphonates.[13-15] In some cases there is a different decomposition route—dialkyl ether and monoalkyl polyfluoroalkenylphosphonofluoridate are formed.[13-15] Elimination of the fluoride anion from trialkoxyfluorophosphonate is evidently

† A similar reaction of pentafluoroazapropene $CF_3N=CF_2$ leads to the formation of stable pentafluoroazapropenyltrialkoxyfluorophosphoranes $CF_3N=CFPF(OR)_3$.[19]

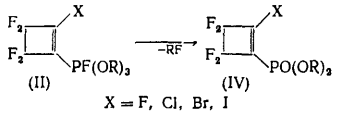
inhibited as a result of the strength of the P–F bond and the elimination of alkoxide anion starts to complete successfully with this reaction. The latter is alkylated by a quasiphosphonium cation and as a result there is a second route for formation of decomposition products—phosphonofluoridate and ether:



For example, when perfluoroisobutenyltriethoxyfluorophosphorane (Ia) is heated to 120–150 °C, ethyl fluoride, diethyl ether, and the perfluoroisobutenylphosphonic acid derivatives—the ester $(CF_3)_2C=CFPO(OEt)_2$ (III) and phosphonofluoridate $(CF_3)_2=CFPF(O)OEt$—are formed.[13]

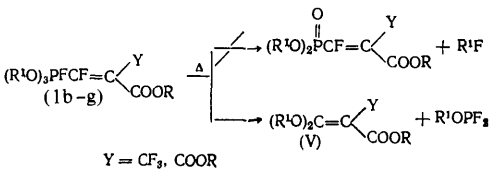
Fluorophosphorane (Ia) is converted to perfluoroisobutenyl phosphonic acid derivatives not only by thermal decomposition but also by hydrolysis. Prolonged reaction with an aqueous solution of sodium bicarbonate gives a mixture of the phosphonic acid $(CF_3)C=CFPO(OH)_2$ and its acid ester $(CF_3)_2C=CFPO(OEt)OH$.[20]

The corresponding phosphonates (IV) are obtained from polyfluorocyclobutenylphosphoranes (II) by heating:[13,14]



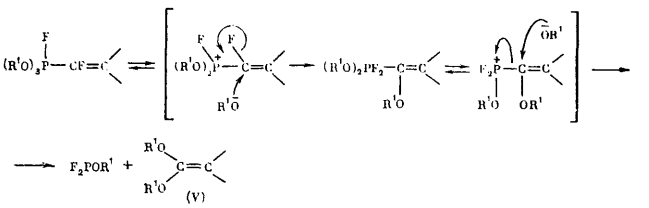
X = F, Cl, Br, I

The alkoxide anion that is formed as an intermediate on decomposition of trialkoxyfluorophosphoranes can, in addition to attacking the alkyl group, react with other electrophilic sites of the molecules, which leads to unusual decomposition of fluorophosphoranes. Thus, pyrolysis of fluorophosphoranes (Ib–g) containing carbalkoxyl groups results in the formation not of fluoroalkenylphosphonates but of acetals of substituted ketones (V) and the trivalent phosphorus compounds—alkyl phosphorodifluoridites:[15,17,18,21]

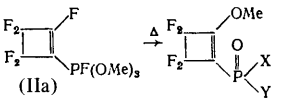


Y = CF_3, COOR

Such a marked difference is probably due to the much greater electrophilicity of the carbon atom in the CF= group in phosphoranes (Ib–g), obtained from perfluoromethacrylates or difluoromethylenemalonates compared to phosphorane (Ia) obtained from perfluoroisobutylene (cf. Ref.22). During pyrolysis it is not the alkyl group but the β-carbon atom of the "acrylic" system that is attacked by the alkoxide anion. As a result of "vinyl" substitution of the geminal fluorine atom a new phosphorane is formed, in which the fluorine atom and alkoxy group have exchanged places. This phosphorane dissociates again into an R^1O^- anion and quasiphosphonium cation; repeated attack by R^1O^- on the β-carbon atom leads to the splitting of the molecule into acetal (V) and alkyl phosphorodifluoridite

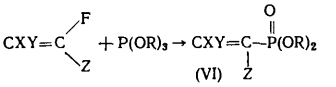


Attack by alkoxide anion on the sp^2-hybridised carbon atom leading to an exchange of substituents between these atoms and the phosphorus atoms has also been detected in the thermal decomposition of perfluorocyclobutenyltrimethoxyfluorophosphorane (IIa).[13,14] However, in this case a vinyl fluorine atom is replaced, the C–P bond does not break, and as a result 2-alkoxytetrafluorocyclobutenyl phosphonic acid derivatives are formed:



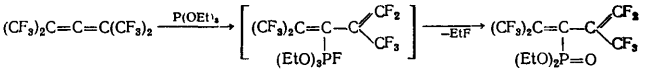
X, Y = F, OMe

In the reactions of fluoroolefins with trialkyl phosphites the fluorophosphoranes formed as intermediates have in a majority of cases not been isolated; heating of the initial compounds gives esters of polyfluoroalkenylphosphonates. Thus, the syntheses of the respective α,β-unsaturated phosphonates (VI) have been reported from tetrafluoroethylene,[20,23,24] trifluorovinyl chloride,[24] trifluorovinyl iodide,[25] perfluoropropylene,‡[23,24,26] perfluoroisobutylene,[23,24] monohydroperfluorobutylene,[27] and ethoxyperfluoroisobutylene:§[27]

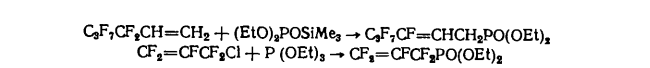


	(a)	(b)		(c)	(d)				(e)	
X=F	F	Cl	I	CF_3	CF_3	CF_3	CF_3	CF_3	CF_3
Y=F	F	F	F	F	F	CF_3	CF_3	F	H	OEt
Z=F	F	F	F	F	F	F	F	F	OEt	OEt
R=Et	iso-Pr	Et	iso-Pr	Et	iso-Pr	iso-Pr	Bu	Et	Et

Reaction of *tetrakis*(trifluoromethyl)allene gives the corresponding 1,3-dienyl-2-phosphonate probably by an S_N2' reaction:[28]



Nonafluorohexene[29] and perfluoroallyl chloride[30] undergo similar reactions:



Trifluorovinyl iodide reacts with $(iso\text{-}PrO)_3P$ or $(EtO)_2POSiMe_3$ to form phosphonate (VIc) or $ICF=CFPO(OEt)_2$. When phosphite is in excess, products derived from substitution of the

‡ In the reaction of perfluoropropylene with triethyl phosphite (130–140 °C), phosphonofluoridate $CF_3CF=CFPF(O)OEt$ is formed in addition to ester (VId).[13]

§ Ethoxyperfluoroisobutylene also shows alkylating properties towards triethyl phosphite.[32]

fluorine and iodide atoms are obtained—*bis*-phosphonates (VII).[25,31] *bis*-Phosphonate (VIIa) is also formed by the action of $(EtO)_2POSi.Me_3$ on tetrafluoroethylene[31]

$$(RO)_2\overset{O}{\overset{\|}{P}}CF=CF\overset{O}{\overset{\|}{P}}(OR)_2,\ R = Et\,(a),\ iso\text{-}Pr\ (b)$$
(VII)

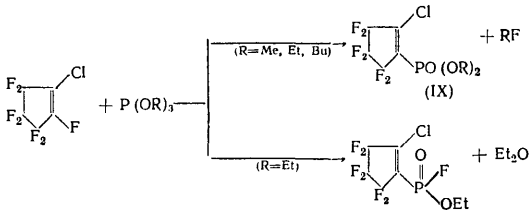
Halogen-substituted polyfluoroalkanes are sometimes used as starting materials for the preparation of polyfluoroalkenylphosphonates:[33,34]

$$RCF(X)-CY_2(Cl) \xrightarrow[-XCl]{P(OEt)_3} [RCF=CY_2] \xrightarrow[-EtY]{P(OEt)_3} RCF=CYPO(OEt)_2$$
(VIII)

$X = F,\ Y = Cl,\ R = CFCl_2;\ X = Cl,\ Y = F,\ R = I(CF_2)_2\,(a),\ I(CF_2)_4\,(b),\ I(CF_2)_6\,(c)$

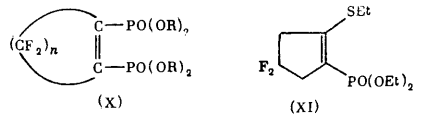
In this case fluoroolefins are evidently formed as intermediates. The formation of the fluoroolefin $CFCl_2CF_2CF=CF_2$ has been demonstrated, for example, in the reaction of 1,2,4,4-tetrachloroperfluorobutane with triethyl phosphite.[3]

1-Chloroperfluorocyclopentene reacts with trialkyl phosphites to give 2-chloroperfluorocyclopenteneylphosphonates (IX). When triethyl phosphite is used, Et_2O and phosphonofluoridate are also formed:[36]



Products from the substitution of both chlorine atoms (X) are obtained from 1,2-dichloroperfluorocycloalkenes.[10] However, reaction of dichloroperfluorocyclopentene with triisopropyl phosphite gives exclusively the monosubstitution product (IX), where R = iso-Pr. Evidently steric hindrance plays an important role in substitution of the second halogen atom.

In the reaction of 1-ethylthio-2-chloroperfluorocyclopentene with triethyl phosphite the corresponding phosphonate (XI) is obtained.

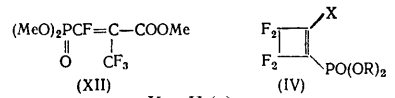


$n = 2-4;\ R = Me, Et, Bu,\ CH_2=CHCH_2$

Neutral phosphonites and phosphinites react with flouroolefins in a similar manner to trialkyl phosphites, giving perfluoroalkenylphosphinates and perfluoroalkenylphosphine oxides.[24,38]

Dialkyl phosphites usually react with fluoroolefins to form addition products.[39] However, in some cases "vinyl" substitution products are also formed. Thus, when perfluoromethacrylate reacts with dimethyl phosphite the unsaturated phosphonate (XII) is obtained.[15] The mechanism of this reaction is not clear. The possibility cannot be excluded that here, as in certain other cases, an addition product is initially formed, then undergoes dehydrofluorination by the action of dialkyl phosphite.

Polyfluorocyclobutenylphosphonates (IV) are formed from polyfluorocyclobutenes and dialkyl phosphites by irradiation.[39]



$X = H\,(a), F, Cl, OR$

Sodium dialkyl phosphite reacts with terminal perfluoroolefins by replacing one of the fluorine atoms in the difluoromethylene group:[8]

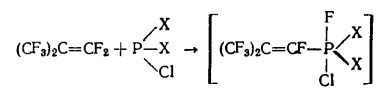
$$R_FCF=CF_2 + NaOP(OEt)_2 \rightarrow R_FCF=CFPO(OEt)_3$$
$$R_F = n\text{-}C_6F_{13},\ n\text{-}C_7F_{15}$$

The substitution of both vinyl fluorine atoms on treatment with salts of acid esters of phosphorus or methylphosphorous acids has been reported for perfluorosiobutylene,[40] in a similar manner to reactions of this fluoroolefin with certain other nucleophiles:[41]

$$(CF_3)_2C=CF_2 + NaOP(X)OR \rightarrow (CF_3)_2C=C[P(O)(X)OR]_2$$
$X = RO, Me$

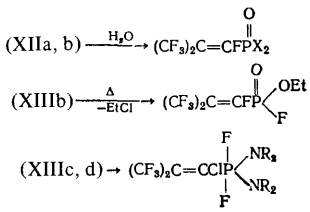
However, there is some doubt about this result since the IR spectra ($\nu_{C=C}$ at 1745 cm^{-1}) are apparently not consistent with the proposed *bis*-phosphonate and *bis*-phosphinate structures.

The vinyl fluorine atom in perfluoroisobutylene is replaced by the action of certain acid chlorides of trivalent phosphorus.[42] The intermediate formation of fluorophosphoranes (XIII) is suggested here:



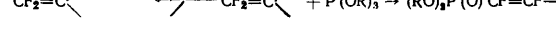
$X = Et\,(a), OEt\,(b), NMe_2\,(c), NEt_2\,(d)$

Dialkyl- and dialkoxy-fluorochlorophosphoranes (XIIIa, b) are hydrolysed with very great ease to the phosphine oxide or phosphonate respectively. For dialkoxy derivative (XIIIb) in the complete absence of moisture the reaction is accompanied by the liberation of alkyl chloride and the formation of phosphonofluoridate. Diamino derivatives (XIIIc, d) are isomerised to α-chloro-substituted difluorophosphoranes:



In this case the fluorine and chlorine atoms exchange places [the mechanism of this reaction is possibly similar to the mechanism for exchange of fluorine atoms and alkoxy groups in the thermal decomposition of trialkoxyfluorophosphoranes (Ib–g), see above].

Thus, reaction of fluoroolefins with phosphites is a general method for the synthesis of fluoroalkenylphosphonates with the olefin double bond in the α,β-position. However, in this case compounds with an internal double bond are formed since the mechanism for "vinyl" substitution in fluoroolefins usually makes these reactions unsuitable for the preparation of "terminal" fluoroalkenylphosphonates containing the $CF_2=\overset{|}{C}-P$ fragment:



An exception to this could be the reaction of trialkyl phosphites with tetrafluoroethylene, which, according to Ref.24, gives trifluorovinylphosphonates (VIa, b). However, these compounds apparently cannot be obtained from tetrafluoroethylene in satisfactory yield, since they readily react further with neutral phosphites[31] (see section III, 2e). The method used for preparing trifluorovinylphosphonates is given in section II, 3.

2. Formation of C=C Double Bond by Elimination

Like their nonfluorinated analogues[1] many fluorine-containing alkenylphosphonates are obtained by dehalogenation or dehydrohalogenation of the appropriate unsaturated halogenated derivatives. Thus, when products of the radical addition of dialkyl phosphites to dichlorodifluoroethylene or trichlorofluoroethylene are treated with zinc in alcohol, fluorine-containing vinylphosphonates are formed:[43,44]

$$CFCl{=}CX_2 + HPO(OR)_2 \rightarrow CHX_2CFClPO(OR)_2 \xrightarrow{Zn} CHX{=}CFPO(OR)_2$$
$$X = F,\ Cl;\ R = Me,\ Et,\ n\text{-}Pr$$

Dechlorination of the dichloro-substituted ester (XIV) with metallic zinc in ether gives an adduct of zinc chloride with unsaturated ester:[45]

$$ClCF_2{-}CCl{-}PO(OMe)_2 \xrightarrow{Zn} CF_2{=}C{-}PO(OMe)_2 \cdot ZnCl_2$$
$$\quad\ CF_3 \qquad\qquad\qquad\quad CF_3$$
$$\quad (XIV)$$

Trihaloethylphosphonates (XV)¶ are fairly readily dehydrochlorinated with triethylamine or potassium *tert*-butoxide to form dihalovinylphosphonates (XVI):[46–48]

$$YCH_2CXPO(OEt)_2 \xrightarrow[-HCl]{} YCH{=}CXPO(OEt)_2$$
$$\quad\ Cl$$
$$\quad (XV) \qquad\qquad\qquad (XVI)$$
$$X,\ Y = F,\ Cl$$

Dehydrofluorination of 2,2-difluoroethylphosphonates using sodium alkoxides gives various 2-fluorovinylphosphonates:[9]

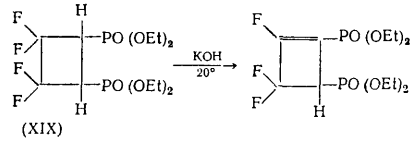
$$HCF_2CH_2PO(OR)_2 \xrightarrow[-HF]{} HCF{=}CHPO(OR)_2$$
$$R = Me,\ Et,\ C_5H_{11}$$

2-Fluorovinylmethylphosphonate is synthesised in the same manner.[9]

Unsaturated α-phosphoryloxyphosphonates (XVIII) are obtained from α-*H*-α-phosphoryloxyphosphonates (XVII):[49]

$$R_FCF_2CH\begin{matrix}OPO(OR)_2\\PO(OR)_2\end{matrix} \xrightarrow{(iso\text{-}Pr)_2NLi} R_FCF{=}C\begin{matrix}OPO(OR)_2\\PO(OR)_2\end{matrix}$$
$$\quad (XVII) \qquad\qquad\qquad\qquad (XVIII)$$

The product (XIX) of the radical addition of diethyl phosphite to 2-monohydroperfluorocyclobutenylphosphonate is dehydrofluorinated with alkali under mild conditions:[39]



(XIX)

For the dehydrofluorination of 2,2,3,3-tetrafluorocyclobutyl phosphonate see section III, 2e.

The reaction of hexafluoroisopropylphosphonates (XX) with $Et_3N.BF_3$ adducts under mild conditions gives pentafluoroisopropenylphosphonates (XXI):[50,51]

$$(CF_3)_2C\begin{matrix}S\\S\end{matrix}C(CF_3)_2 \xrightarrow{P(OR)_3} (CF_3)_2C{=}P(OR)_3 \xrightarrow{HCl} (CF_3)_2CHPO(OR)_2 \rightarrow$$
$$\quad (XXII) \qquad\qquad\qquad\quad (XX)$$
$$\xrightarrow[-Et_3\overset{+}{N}H\ \bar{B}F_4]{Et_3N\cdot BF_3} CF_2{=}C{-}PO(OR)_2$$
$$\qquad\qquad\qquad\qquad\quad CF_3$$
$$\qquad\qquad\qquad\quad (XXI)$$
$$R = Me\ (a),\ Et\ (b)$$

Apart from 1,2-elimination of halogens or hydrogen halides, fluoroalkenylphosphonates can be obtained by 1,4-elimination of alkyl fluorides from P-alkoxy-substituted fluorine-containing phosphorus ylides. When hexafluoroisopropylidenetriethyoxyphosphorane (XXIIb) is heated with a catalytic quantity of boron trifluoride etherate, ethyl fluoride, and pentafluoroisopropenylphosphonate (XXIb)† are formed:[51]

$$(CF_3)_2C{=}P(OEt)_3 \xrightarrow{Et_2O\cdot BF_3} CF_2{=}C{-}PO(OEt)_2 + EtF$$
$$\qquad\qquad\qquad\qquad\qquad\quad CF_3$$
$$\quad (XXIIb) \qquad\qquad\qquad (XXIb)$$

This reaction is similar to the conversion of alkoxypolyfluoroisobutylenes $(CF_3)_2C{=}CXOR$ to perfluoromethacrylic acid derivatives

$$CF_2{=}CCOX$$
$$\quad CF_3 \qquad [21].$$

1,4-Elimination of alkyl fluoride evidently occurs in stages. Initially the Lewis acid (BF_3) removes a fluoride anion from the phosphorus ylide to form an unstable adduct (XXIII) containing a mesomeric cation. This adduct readily decomposes to ethyl fluoride and an adduct (XXIV) of unsaturated phosphonate with boron trifluoride. The latter is converted to the final product—free phosphonate (XXIb) by the action of another molecule of phosphorus ylide (XXIIb), which in the process again gives adduct (XXIII), and so on:[51]

$$(XXIIb) \xrightarrow{BF_3} CF_2{\cdots}\overset{+}{C}{\cdots}P(OEt)_3\ \bar{B}F_4 \xrightarrow[-EtF]{} CF_2{=}C{-}PO(OEt)_2\cdot BF_3 \rightarrow$$
$$\qquad\qquad\quad CF_3 \qquad\qquad\qquad\qquad\quad CF_3$$
$$\qquad\qquad (XXIII) \qquad\qquad\qquad (XXIV)$$
$$\xrightarrow{(XXIIb)} CF_2{=}C{-}PO(OEt)_2 + (XXIII)$$
$$\qquad\qquad\quad CF_3$$
$$\qquad\qquad (XXIb)$$

Each stage of this scheme has been confirmed experimentally.

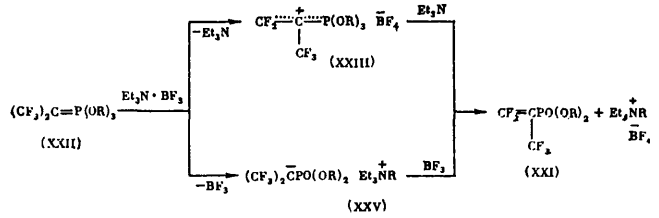
The *bis*-trimethylsilyl ester of pentafluoroisopropenylphosphonic acid (XXIc) is obtained by the direct reaction of *tris*(trimethylsilyl) phosphite with hexafluorothioacetone dimer, and also from phosphorus ylide (XXIIa) and trimethylsilyl iodide:[52]

$$(CF_3)_2C\begin{matrix}S\\S\end{matrix}C(CF_3)_2 \xrightarrow[-(Me_3SiO)_4PS]{(Me_3SiO)_3P} [(CF_3)_2C{=}P(OSiMe_3)_3] \xrightarrow{-Me_3SiF}$$
$$(CF_3)_2C{=}P(OMe)_3 \xrightarrow[-MeI\ -Me_3SiF]{Me_3SiI} CF_2{=}C{-}PO(OSiMe_3)_2$$
$$\qquad\quad (XXIIa) \qquad\qquad\qquad\qquad\quad CF_3$$
$$\qquad\qquad\qquad\qquad\qquad\quad (XXIb)$$

¶ Obtained as mixtures of stereoisomers by treatment of the olefins FCH=CHF and FCH=CHCl with phosphorus trichloride and oxygen and subsequent ethanolysis of the reaction mixture.[48]

† Under similar conditions trimethoxyphosphorane $(CF_3)_2C{=}P.(OMe)_3$ (XXIIa) rearranges to the saturated phosphonate $(CF_3)_2C.(Me)PO(OMe)_2$.[51]

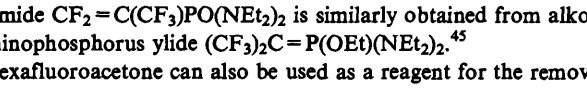
It seems that the most convenient method for obtaining pentafluoroisopropenylphosphonic acid derivatives is removal of alkyl fluoride from phosphorus ylides (XXII) with an equimolar quantity of $Et_3N.BF_3$ adduct:[51]



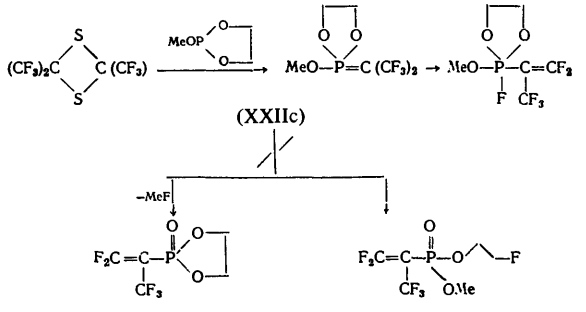
In the process tetraalkylammonium fluoroborates are formed together with phosphonates (XXI). The reaction may occur by one of two pathways. The first of them assumes an initial elimination of fluoride ion to give adduct (XXIII) followed by the transfer of alkyl to amine, the second assumes initial dealkylation followed by elimination of fluoride ion from the mesomeric carbanion of tetraalkylammonium salt (XXV).[51]

Amide $CF_2=C(CF_3)PO(NEt_2)_2$ is similarly obtained from alkoxydiaminophosphorus ylide $(CF_3)_2C=P(OEt)(NEt_2)_2$.[45]

Hexafluoroacetone can also be used as a reagent for the removal of alkyl fluoride. When it is heated with trialkoxyphosphoranes (XXIIa, b), alkyl perfluoroisopropyl ethers and unsaturated phosphonates (XXIa, b) are formed:[51]



In contrast to trialkoxyphosphorus ylides (XXIIa, b), 2-(hexafluoroisopropylidene)-2-methoxy-1,3,2$\lambda^5\sigma^4$-dioxaphospholan (XXIIc) does not eliminate alkyl fluoride but rearranges under mild conditions to 2-(pentafluoroisopropenyl)-2-fluoro-2-methoxy-1,3,2$\lambda^5\sigma^4$- dioxaphospholan:[53]

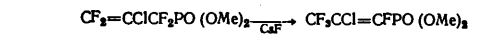


The methods based on elimination of halogens, hydrogen halides, or alkyl halides from saturated phosphonates or alkoxyphosphorus ylides have considerable potential for the preparation of fluoroalkenyl phosphonates, although they have not so far been developed to a sufficient extent. It should be emphasised that when these methods are used both "internal" and "terminal" fluoroalkenylphosphonates can be obtained.

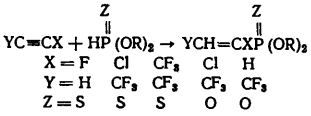
3. Other Methods

Apart from the two main synthetic methods described above, fluoroalkenylphosphonates can also be obtained by a variety of methods, which are based on the introduction of a fluorine atom, formation of a C–P bond, formation of a C=C bond by means of Wittig–Horner reactions, various rearrangements, etc.

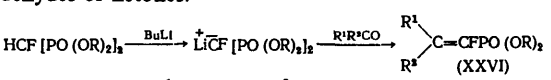
2-Chlorotetrafluoropropenylphosphonate is obtained by rearrangement of 2-chlorotetrafluoroallylphosphonate:[54]



Treatment of fluorine-containing acetylenes with acid phosphites and phosphorothioites gives the corresponding fluoroalkenylphosphonates and fluoroalkenylthiophosphonates:[55]

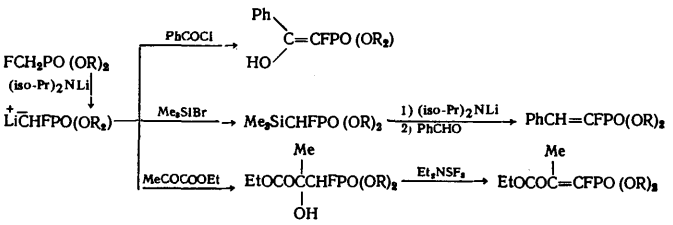


The Wittig–Horner reaction is used to obtain α-fluorovinylphosphonates (XXVI) from tetraalkyl fluoromethylene-*bis*-phosphonates and aldehydes or ketones:[56]

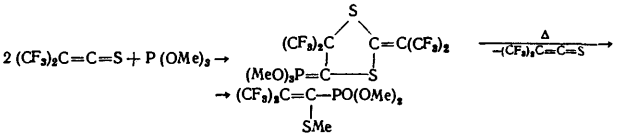


R = iso-Pr; R^1 = H, Me; R^2 = H, Me, iso-Pr, Ph, etc.

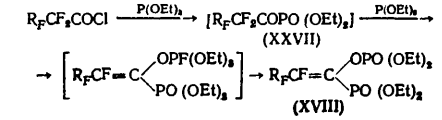
The lithium derivative obtained from dialkyl fluoromethylphosphonate is also used for the synthesis of unsaturated α-fluorophosphonates:[57]



Reaction of *bis*(trifluoromethyl)thioketen with trimethyl phosphite gives α-methylthioperfluoroisobutenylphosphonate:[58]

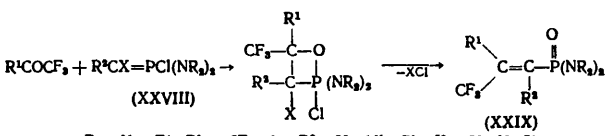


An interesting method for obtaining α-substituted fluorine-containing alkenylphosphonates (XVIII) is that based on the reaction of perfluorocarboxylic acid chlorides with triethyl phosphite:[49,59–62]



Acylphosphonate (XXVII) formed as an intermediate cannot be isolated from the reaction as it immediately undergoes a rapid reaction with another molecule of phosphite. The mobility of the phosphate group in compounds (XVIII) opens up extensive possibilities of synthesising various organofluorine compounds either containing or not containing a phosphorus atom (see below).

The reaction of chlorophosphonium ylides (XXVIII) with fluoroketones gives fluoroalkenylphosphonic acid amides (XXIX):[63–64]

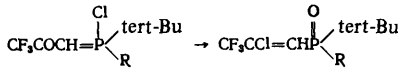


R = Me, Et; R^1 = CF_3, Ar; R^2 = H, Alk, Ph; X = H, Me_3Si

P-Chloro-substituted oxaphosphetans are formed in the process as intermediates.

Phosphinic acid amides and phosphine oxides are obtained in a similar manner.[63–66]

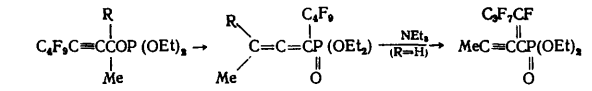
Chlorophosphonium acylmethylides undergo an interesting rearrangement:[67]



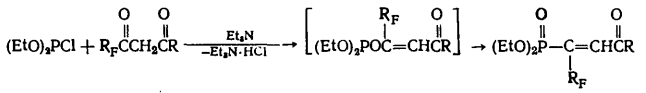
R = tert-Bu, NEt_2

The oxygen and chlorine atoms exchange places as a result of reaction.

Rearrangement of diethyl alkynyl phosphites (XXX) gives fluorine-containing allenylphosphonates; when R = H a further dehydrofluorination is possible:[68]

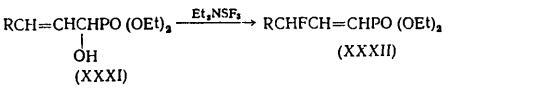


Reaction of fluorine-containing β-diketones with diethyl phosphorochloridite leads to the synthesis of α-perfluoroalkyl-γ-keto-vinylphosphonates, which are probably formed by rearrangement of the corresponding phosphites:[69]

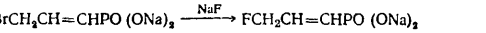


$R_F = CF_3$, C_3F_7; R = Me, tert-Bu

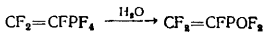
Monofluoroalkenylphosphonate derivatives can be obtained from unsaturated phosphonate compounds by standard reactions for the introduction of fluorine atoms. Thus, fluoroalkenylphosphonates (XXXII) are synthesised by treatment of hydroxyphosphonates (XXXI) with (N-ethylethanaminato)trifluorosulphur (DAST).[70]



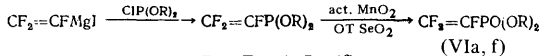
The salt of 3-fluoropropenylphosphonic acid is obtained by the replacement of a bromine atom with a fluorine atom:[71]



When $C_2F_5SiF_3$ is pyrolysed in the presence of PF_3, trifluorovinyltetrafluorophosphorane is formed, hydrolysis of which gives trifluorovinylphosphonic difluoride:[72]



Reaction of trifluorovinylmagnesium iodide with dialkyl phosphorochloridates followed by oxidation of the phosphonites formed gives trifluorovinylphosphonates (VIa, f):[31]

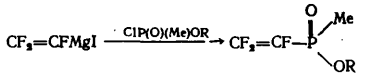


R = Et (a), Bu (f)

A similar sequence of reactions has been used previously to synthesise vinylphosphonates.[73]

The direct formation of phosphonates $RPO(OR^1)_2$ from organometallic compounds RM and dialkyl phosphorochloridates $ClPO.(OR^1)_2$ is usually complicated by side reactions.[3] It was not possible to obtain trifluorovinylphosphonate (VIa) by reaction of trifluoromagnesium iodide with diethyl phosphorochloridate.[45]

However, the preparation of trifluorovinylmethylphosphinates by reaction of trifluorovinylmagnesium iodide with alkyl methylphosphonochloridates has been reported:[40]

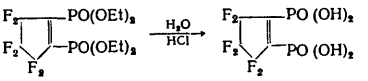


Among the methods for obtaining fluoroalkenylphosphonic acid derivatives it is also possible to include many reactions of those compounds which lead to products in which the C=C bond and $P(O)X_2$ group are retained. These reactions together with other conversions of fluoroalkenylphosphonates are examined in the next chapter.

III. CHEMICAL PROPERTIES

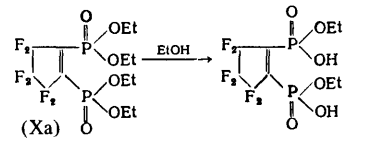
1. Modification of Phosphonate Groups

Fluorine-containing unsaturated phosphonate esters and also phosphinate esters are converted in the usual way to free acids by acid hydrolysis,[36,74–77] for example:



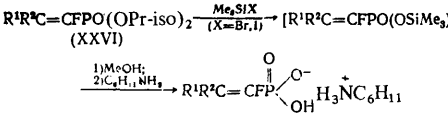
(Xa)

When *bis*-phosphonate (Xa) is boiled with ethanol, *bis*-phosphonic acid ester is formed:[74, 75]

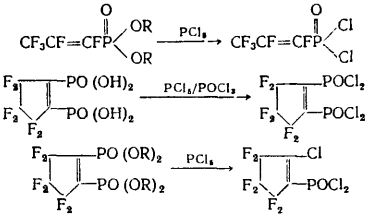


(Xa)

For the conversion of α-fluoroalkenylphosphonates (XXVI) to the corresponding acids, a reaction with trimethylsilyl halides is used followed by alcoholysis (the acids are isolated as their cyclohexylammonium salts):[56]

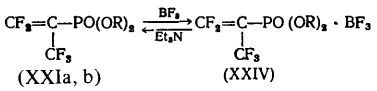


Reaction of fluoroalkenylphosphonic acids or their esters with phosphorus pentachloride gives the corresponding acid chlorides.[13,36,38,74,75] In the case of *bis*-phosphonates replacement of one of the phosphonate groups by a chlorine atom also sometimes occurs:[36,74]



The chlorine atoms in fluoroalkenylphosphonic acid chlorides can be replaced with fluorine atoms in the usual way by treatment with SbF_3 [13] and replaced with hydroxy or alkoxy groups by treatment with water or alcohol.[36,74–76]

Despite the high electrophilicity of the pentafluoroisopropenyl residue, the phosphoryl group in pentafluoroisopropenylphosphonates displays its own basic properties. Esters (XXI) readily form adducts with the Lewis acids $ZnCl_2$ (see section II,2) and BF_3. When treated with triethylamine, the BF_3 adduct (XXIV) is converted to free phosphonate (XXI):[51]



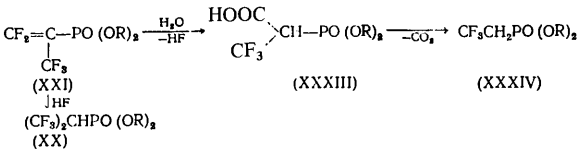
(XXIa, b) (XXIV)

2. Reactions Involving the Fluoroalkenyl Group

The electron-withdrawing effect of the phosphonate groups and fluorine atoms causes the C=C bond in fluoroalkenylphosphonates to have considerable electrophilicity. Hence they react quite readily with various nucleophiles, giving products from the substitution of the halogen atoms on the sp^2-hybridised carbon atom or addition products on the C=C bond.‡ There is considerable interest in the conversions that lead to cleavage of the C–P bond; these sometimes prove to be convenient methods for the synthesis of organofluorine compounds. Reactions with electrophiles are generally less typical for fluoroalkenylphosphonates, although there are examples of addition of halogens and hydrogen halides to the C=C bond.

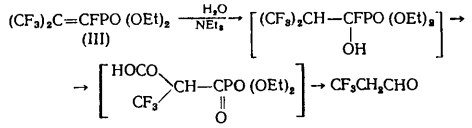
(a) Reactions with Water, Alcohols, and Amines

The highly electrophilic pentafluoroisopropenylphosphonates (XXI), the "phosphoric analogues of perfluoromethacrylates"§ readily react with water, and as a result of hydrolysis of the difluoromethylene group form unstable carboxyphosphonates (XXXIII), decarboxylation of which give trifluoroethylphosphonates (XXXIV):[80]



The reaction is complicated by the fact that the initial unsaturated phosphonate adds on liberated hydrogen fluoride to give dialkyl hexafluoroisopropylphosphonate (XX).

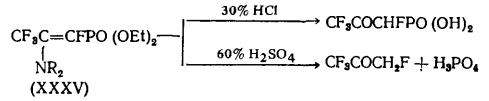
The less electrophilic perfluoroisobutenylphosphonate (III) reacts with water in the presence of triethylamine and is converted to trifluoropropionaldehyde, with the addition product of water to the multiple bond probably being formed as an intermediate:[27]



In this case the orientation for addition of water is determined by the strong electron-withdrawing action of the two trifluoromethyl groups (see below).

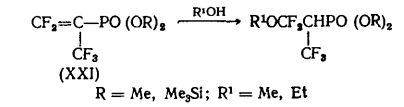
When perfluoroalkenylphosphonates are treated with aqueous alkalis, the fluorine atoms are removed as anions. By determining the quantity of fluoride anions eliminated, Knunyants, Sterlin, et al.[24] conclude that in the reaction of trifluorovinylphosphonate the C–P bond is preserved, while for pentafluoropropenyl- and perfluoroisobutenyl-phosphonates a "haloform" decomposition occurs.

In contrast to perfluoroalkenylphosphonates, enaminophosphonate (XXXV) is readily hydrolysed in acidic medium, with either ketophosphonic acid or tetrafluoroacetone being formed depending on the conditions:[27]



(XXXV)

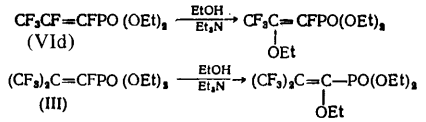
Pentafluoroisopropenylphosphonates (XXIa, c) react with alcohols under mild conditions to form addition products—α-*H*-β-alkoxypentafluoroisopropylphosphonates:[45,52,80]



On the other hand, trifluorovinylphosphonate (VIa) does not react with alcohol even after prolonged heating (~100 °C).[31]

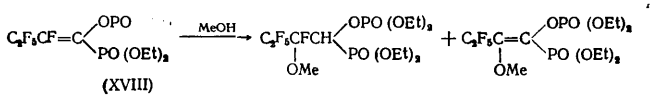
The completing reaction of pentafluoroisopropenylphosphonate (XXIa) and methyl perfluoromethacrylate has been used to demonstrate that these compounds have similar reactivity.[80]

Pentafluoropropenylphosphonate (VIa) and pentafluoroisobutenylphosphonate (III) react with ethanol in the presence of triethylamine.¶ In the first case a vinyl fluorine atom at the β-position is replaced by an alkoxy group, in the second case a fluorine atom at the α-position is replaced:[27]



Here, as in the reactions with water and secondary amines (see below) the direction of nucleophilic attack depends on the competition between the trifluoromethyl and phosphonate groups for conjunction with the C=C double bond; one CF_3 group cannot compete effectively with the $PO(OR)_2$ group, but the electron-withdrawing effect of two trifluoromethyl groups can "overcome" the effect from the $PO(OR)_2$ group.†[27]

α-Phosphoryloxy-substituted perfluoroalkenylphosphonate (XVIII) reacts with methanol to form a mixture of addition and substitution products:[59]



(XVIII)

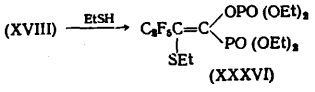
‡ Nucleophilic additions to nonfluorinated alkenylphosphonates have become widely known.[1] However, vinylphosphonates are somewhat less reactive than the analogous acrylates.[78,79]

§ See Ref.21 concerning the electrophilicity of perfluoromethacrylates.

¶ In the reaction of (III) with ethanol in the presence of EtOK, the fluorine atoms are completely eliminated as anions.[27]

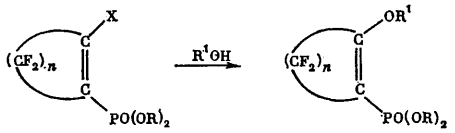
† For a similar competition between trifluoromethyl groups and carbalkoxyl groups, see Ref.81.

However, in the reaction with mercaptan only the product (XXXVI) from substitution of the vinyl fluorine atom is obtained.[59]

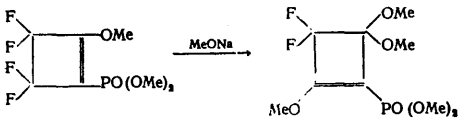


(XXXVI)

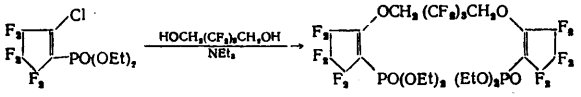
Reaction of unsaturated cyclic fluorine-containing phosphonates with alcohols leads to replacement of the vinyl halogen atoms.[14,39,82] Further substitution of the allyl fluorine atoms by alkoxy groups is also possible:[14]



$n = 2,3$; X = F, Cl, Br

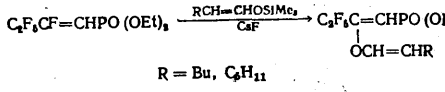


2-Chloroperfluorocyclopentenylphosphonate reacts with hexafluoropentanediol in the presence of triethylamine to form *bis*-phosphonate:[82]



In free 2-chloroperfluorocyclopentenylphosphonic acid the chlorine atom is stable towards the action of bases.[82]

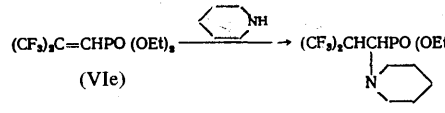
Replacement of a vinyl fluorine atom by a vinyloxy group occurs when α-*H*-perfluorobutenylphosphonate reacts with trimethylsilyl enol ethers:[83]



R = Bu, C_6H_{11}

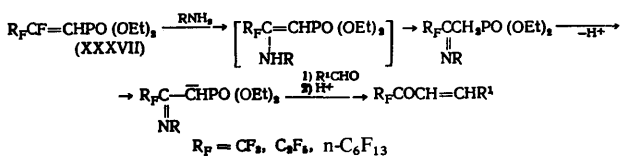
In the reactions of fluoroalkenylphosphonates with amines, depending on the structure of the initial compounds addition products are formed or substitution of the vinyl halogen atom or further conversions occur.

α-*H*-perfluoroisobutenylphosphonate (VIe) adds on a piperidine molecule to the double bond, with the nucleophile attacking the α-position:[27]



(VIe)

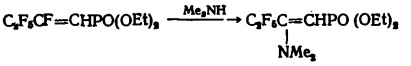
α-*H*-Perfluoroalkenylphosphonates (XXXVII) react with primary amines to form the corresponding imino derivatives evidently by substitution of the vinyl fluorine atom and subsequent rearrangement of the enaminophosphonates:[59]



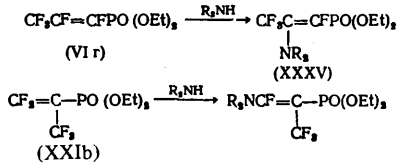
$R_F = CF_3$, C_2F_5, n-C_6F_{13}

Reaction of iminophosphonates with bases gives carbanions that can undergo the Wittig–Horner reaction with aldehydes.[59]

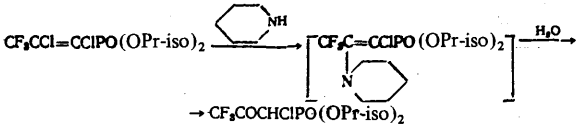
A β-Enaminophosphonate is obtained by the reaction of α-*H*-perfluorobutenylphosphonate with dimethylamine:[59,84]



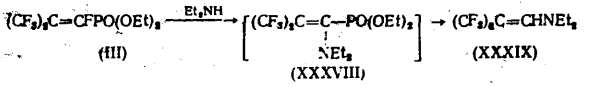
Products from the substitution of the vinyl β-halogen atoms are obtained from pentafluoropropenylphosphonate (VId)‡[38] and pentafluoroisopropenylphosphonate (XXIb):[80]



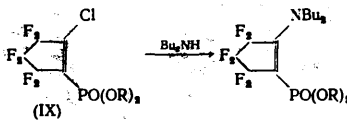
It is reported in one patent[71] that substitution of a vinyl chlorine atom occurred when 1,2-dichloro-3,3,3-trifluoropropenylphosphonate was treated with piperidine; subsequent hydrolysis gave a ketophosphonate:



Reaction of perfluoroisobutenylphosphonate (III) with diethylamine apparently leads to substitution of a vinyl fluorine atom in the α-position, but the unstable enaminophosphonate (XXXVIII) decomposes when treated with excess amine to form enamine (XXXIX):[27]



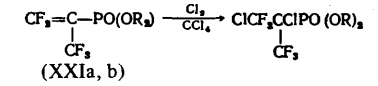
Reaction of unsaturated cyclic phosphonates (IX) with secondary amines gives the corresponding enaminophosphonates:[82]



(IX)

(b) Halogenation and Hydrohalogenation

The electrophilic addition of halogens and hydrogen halides to the C=C double bond is usually hindered when electron-withdrawing groups are introduced into an unsaturated compounds.[85,86] However, despite their high electrophilicity pentafluoroisopropenylphosphonates (XXIa, b) very readily add on chlorine in an inert solvent, and the reaction does not require base catalysis:[87]



(XXIa, b)

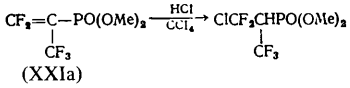
The less electrophilic trifluorovinylphosphonate (VIa) is chlorinated under these conditions much more slowly, which is demonstrated by means of a competing reaction.[31]

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‡ Methyl(pentafluoropropenyl)phosphinate reacts in a similar way.[38]

It is suggested that the phosphonate group acts as an "internal base" which activates the halogen molecule and transfers the halogenation of the highly electrophilic unsaturated compound to a "nucleophilic pathway".[87]

For a similar reason pentafluoroisopropenylphosphonate (XXIa) readily forms an addition product with hydrogen chloride:§[87]



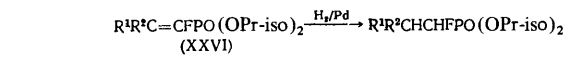
(XXIa)

In these reactions pentafluoroisopropenylphosphonates behave similarly to perfluoromethacrylic acid dialkylamides (cf. Ref.21).

2-Chloroperfluorocyclopentenylphosphonate (IX), when R = Et, decolorises a solution of bromine, while *bis*-phosphonate (X), n = 3, R = Et, does not react with bromine.[77] When tetraallyl perfluorocyclopentenylene-*bis*-phosphonate is brominated, only the C=C bonds in the nonfluorinated allyl fragments react.[10,75]

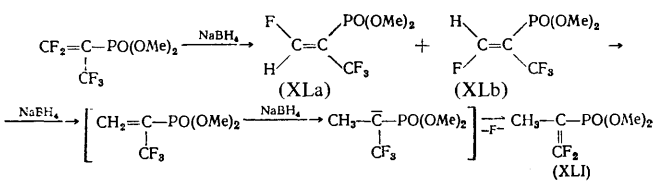
(c) Reduction and Oxidation

The C=C double bond in fluoroalkenylphosphonate derivatives can be saturated by hydrogenation and oxidation. α-Fluorovinylphosphonates (XXVI) undergo catalytic hydrogenation to give the corresponding phosphonates:[56]



(XXVI)

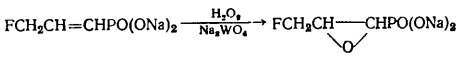
Reaction of pentafluoroisopropenylphosphonate (XXIa) with sodium borohydride leads to replacement of fluorine atoms by hydrogen. The monohydro derivatives (XLa, b) and trihydro derivatives (XLI) have been identified among the reaction products:[45]



(XLa) (XLb)

(XLI)

The formation of the α-oxide from 3-fluoropropenylphosphonate salt has been reported:¶[71]

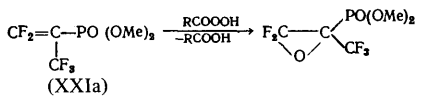


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§ Chlorine-containing alkynylphosphonates react in a similar manner with hydrogen chloride.[88]

¶ Oxides of nonfluorinated unsaturated phosphonates can be obtained by various methods including epoxidation. Propenylphosphonic acid oxide $CH_3CH\!-\!CHPO(OH)_2$ (phosphonomycin) is an antibiotic.[91]

Pentafluoroisopropenylphosphonate (XXIa) is readily epoxidised when treated with an aromatic peroxyacid in ether:[89,90]



(XXIa)

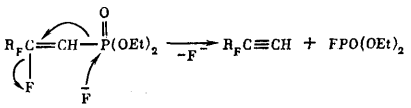
Perfluoromethacrylic acid derivatives behave in a similar manner.[21,89]

2-Chloroperfluorocyclopentenylphosphonate (IX), where R = Et, decolorises a solution of permanganate.[77]

(d) Reactions with Fluoride Ion

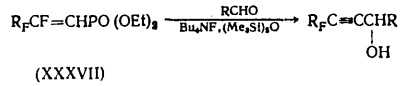
Attack by a fluoride ion can be directed on to either the phosphorus atom or an electrophilic carbon atom of a fluoroalkenylphosphonate depending on its structure.

Thus, α-*H*-perfluoroalkenylphosphonates (XXXVII) when treated with a catalytic quantity of tetrabutylammonium fluoride or caesium fluoride are converted to perfluoroalkylacetylenes:[60,83]



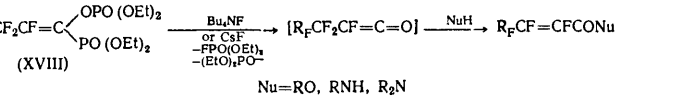
(XXXVII)

In the presence of aldehydes, ethynylcarbinols are formed:[92]



(XXXVII)

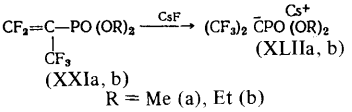
For phosphoryloxyphosphonates (XVIII) cleavage of the C–P bond is also possible. Combined treatment with fluoride anion and alcohol or amine gives α,β-unsaturated carboxylic acid derivatives, with fluorine-containing ketenes probably formed as intermediates:[93]



(XVIII)

Nu=RO, RNH, R_2N

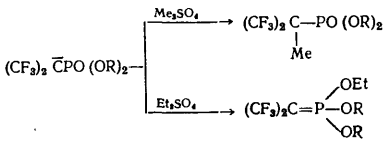
The highly electrophilic pentafluoroisopropenylphosphonates (XXI) add on an F^- anion to the C=C double bond under mild conditions. Treatment with CsF in polar aprotic solvents at low temperatures gives relatively stable solutions of salts (XLII), which contain an α-phosphonate-substituted carbanion:[80]



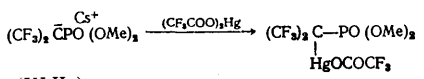
(XXIa, b) (XLIIa, b)

R = Me (a), Et (b)

This mesomeric carbanion can be alkylated on either the carbon atom or oxygen atom:[80]

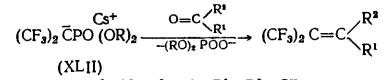


The mercuration of salt (XLIIa) has also been reported:[45]



(XLIIa)

There is considerable interest in the use of salts (XLII) in the Wittig–Horner reaction. On treatment with carbonyl compounds, fluorine-containing olefins are formed:[80]



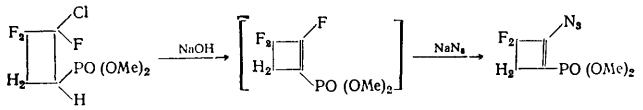
(XLII)

R^1=H, R^2=Ph; R^1=R^2=CF_3

In the Wittig–Horner reaction here a nonstandard method is used to obtain the initial α-phosphonate-substituted carbanion. Instead of the usual deprotonation of α-*H*-phosphonate,[94] use is made of the addition of a nucleophile (F^-) to an α,β-unsaturated phosphonate.†

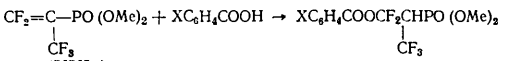
(e) Other Reactions

The action of sodium azide in the presence of alkali on cyclic phosphonate (XLIII) gives an unsaturated azidophosphonate, probably as a result of substitution of the vinyl fluorine atom in the cyclobutenylphosphonate (XLIV) formed as an intermediate:[96]



(XLIII) (XLIV)

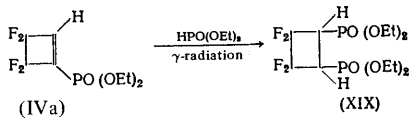
In a similar manner to perfluoromethacrylates,[21,89] pentafluoroisopropenylphosphonate (XXIa) readily adds on carboxylic acids:[80]



(XXIa)

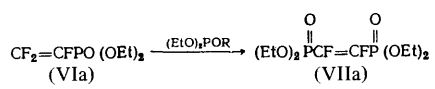
X=H, *m*-Cl

The reaction of 2-*H*-perfluorocyclobutenylphosphonate (IVa) with diethyl phosphite occurs under conditions for radical formation and gives addition product (XIX):[39]



(IVa) (XIX)

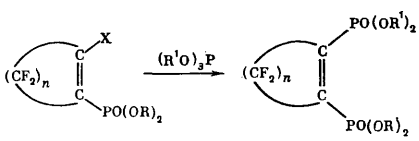
When trifluorovinylphosphonate (VIa) is reacted with neutral phosphites, a vinyl fluorine atom is replaced and *bis*-phosphonate (VIIa) is formed:[31]



(VIa) (VIIa)

R=Et, Me_3Si

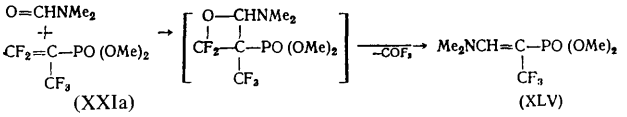
A similar substitution of the vinyl halogen atom also occurs for cyclic unsaturated phosphonates:[14,74]



n=2,3; X=Cl, Br, I

ω-Iodoperfluoroalkenylphosphonates (VIIIa–c) do not react with triethyl phosphite even on heating.[34]

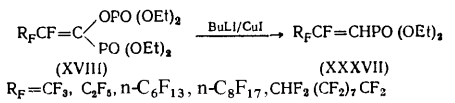
Pentafluoroisopropenylphosphonate (XXIa) reacts with dimethylformamide to give enaminophosphonate (XLV), probably through the intermediate formation of a cycloadduct:[80]



(XXIa) (XLV)

The analogous reactions of perfluoromethacrylic acid derivatives have been widely reported.[21]

α-Phosphoryloxy-substituted phosphonates (XVIII) when treated with butylcopper are converted to α-*H*-perfluoroalkenylphosphonates (XXXVII):[61]



(XVIII) (XXXVII)

R_F=CF_3, C_2F_5, n-C_6F_{13}, n-C_8F_{17}, $CHF_2(CF_2)_7CF_2$

* * *

In the summary presented above the variety of reactions of fluoroalkenylphosphonates, which combine the properties of fluorine-containing olefins and phosphonic acid derivatives, should be noted. There is definite interest in a systematic study of this class of compounds especially since some of them may have practical application.

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† Addition of mercaptides to α-alkoxycarbonylvinylphosphonates has been used in the same way.[95]

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The Use of Electrochemical Methods for Studying the Structure and Reactivity of Organometallic Compounds

T.V.Magdesieva, K.P.Butin, and O.A.Reutov

The different aspects of using electrochemical methods for studying the structure and reactivity of organometallic compounds as well as for investigating certain details of their reaction mechanisms such as regioselectivity, process compatibility, the role of nucleophilic assistance, and so forth are examined.
The bibliography includes 95 references.

CONTENTS

I. Introduction 864
II. Redox processes in which electron changes are localised on the metal atom 865
III. Redox processes in which electron changes are localised on the π-bond orbitals 867
IV. Redox processes in which electron changes are localised on the σ-bond orbitals 868
V. Simultaneous calculation of electrochemical oxidation and reduction potentials of organometallic compounds in order to determine their reactivity 870

I. INTRODUCTION

In recent years electrochemical methods have become more widely used not only for the purposes of analysis but also for studying the structure and reactivity of organic molecules.[1,2] Electrode reactions can be regarded as models of the fundamental stages of a large number of organic reactions, above all redox reactions.[3]

However, electrochemical methods, apart from classical polarography and cyclic voltammetry, are still not sufficiently popular among organic chemists and organometallic chemists although their relative simplicity to use in terms of equipment could be very useful for solving such theoretical and practical questions as: 1) quantification of redox properties of compounds; 2) determination of the electronic effects of substituents 3) the use of half-wave potentials ($E_{1/2}$) for oxidation and reduction in quantum chemical calculations, including those for determining the site of localisation of electron changes in the molecule during redox reactions; 4) the study of processes leading to the formation of unstable products such as radicals and radical ions; 5) studying the mechanism (kinetics, stoichiometry) of the electrochemical process as a model of the fundamental event of a chemical reaction; 6) establishing a correlation between $E_{1/2}$ for reduction of the M−R σ-bond and the properties of the carbanion R^- or radical R, such as the acidity of RH, nucleophilicity of R^-, electron affinity of R, and so on; 7) the choice of conditions for electrosynthesis of organic and organometallic compounds.

Half-wave potentials are not standard redox potentials in the strict thermodynamic sense. They also include kinetic, adsorption, solvation, and other effects. Nevertheless, they characterise sufficiently precisely the redox properties of a vast number of organic molecules in solution and are often the only available numerical indicators of these properties. Values of $E_{1/2}$, to a greater degree than many other physicochemical quantities, are sensitive to electronic effects in molecules but reflect the spatial configuration and conformation of organic molecules less precisely.

Electrochemical methods can be successfully used to study heterolytic reactions in which the key stage is transfer of an electron from donor to acceptor. Specific criteria have been developed[4] for electrochemical modelling of the fundamental event of a chemical reaction.

1. In drawing an analogy between chemical and electrochemical reactions it is necessary that the same products are obtained as a result of their taking place.
2. After the electron transfer has been defined in a chemical reaction, it is necessary to introduce products formed from electron donors or acceptors into the solutions intended for electrochemical studies and to model their action using electrochemical methods.
3. If the reversibility of the events of electron transfer for the reagents studied can be demonstrated using electrochemical methods and EPR can be used to identify radical ions that are formed in electrochemical and chemical reactions, it may be assumed that the radical ions are sufficiently stable and that the rate of reaction is determined by the slow stage of their decomposition, after which σ-radicals are formed.
4. It should be taken into account that a change in the type of medium can produce a marked change in reaction mechanism and this is clearly defined using electrochemical methods.

It is necessary to take great care when considering the possibilities of using polarography for quantitative determination of the structure and reactivity of organic molecules. It is usually recommended that irreversible waves are immediately excluded from consideration, since the subsequent reactions of radical ions also contribute to their potentials. Two-electron waves are also unsuitable because in the majority of cases transfer of two electrons is due to rapid chemical reactions in the vicinity of the electrode. Consequently, consideration can only be given to reversible one-electron waves for oxidation or reduction, but in this case the heterogeneous nature of the electrode reaction and the specific interaction of substrate with reagent that precedes the transfer of an electron, etc, should be borne in mind. Therefore $E_{1/2}$ values may only reflect a general trend in the change of properties and are relative values. In this connection Okhlobystrin[5] has criticised Pozharskii,[6] who had proposed the use of polarography "as a guiding principle in quantitative studies on reactivity." Nevertheless, even a purely qualitative approximate assessment of the properties of compounds based on electrochemical data can often be very useful.

There have recently been a number of reviews and monographs published on the electrochemistry of heteroorganic compounds such as derivatives of nontransition elements,[7,63] Group I-III elements and transition metals,[8,9] and also metal chelates.[10,11] Aspects of electrochemical synthesis have been examined in reviews.[12,13] Works

devoted to studying π-complexes of transition metals have been correlated in reviews.[14,15] The increased interest in these compounds is due to the fact that the majority of them readily undergo redox conversions that occur with a change in formal oxidation state of the metal while retaining the structure of the organometallic compound and also because the values of the half-wave potentials lie in a convenient region to study. Moreover, processes in which cleavage of C−M or M−X σ−bonds does not occur, are, as a rule, reversible, which increases the strictness of the correlations obtained.

In the present review we examine the works of those authors who do not confine themselves to measuring redox potentials of a given compound and determining the products of their electrochemical conversions but use electrochemical data to study the electronic structure of molecules and predict their chemical properties. The subject matter is arranged in accordance with the site of localisation of electron changes during chemical and electrochemical redox reactions of π- and σ-organometallic compounds, the method for determination of this being proposed in [16].

II. REDOX PROCESSES IN WHICH ELECTRON CHANGES ARE LOCALISED ON THE METAL ATOM

If the metal atom in a complex is bonded by a delocalised π-bond only to carbocyclic ligands and has an electron shell similar to the atoms of an inert gas, when redox processes occur the electron changes are localised on the metal atom. Reactions such as this have the following characteristics: 1) the electron configurations of the oxidised and reduced forms are similar and the electrode reaction is reversible; 2) potentials are virtually independent of the solvent; 3) the polarographic properties do not depend on the addition of a proton donor:

The system ferrocene−ferrocenium ion is very convenient for study, as it is firstly, reversible and, secondly, the rate of its electron exchange is high. The electrochemical behaviour of this system and also π-complexes of other metals has been examined in reviews,[14,15] so we will not go into this subject in detail. The first attempts to establish correlations between the reactivity of organic compounds and the half-wave potentials for their oxidation or reduction date back to the beginning of the 1950s, when the linear free energy principle (equations of Hammett, Taft, Yukawa−Tsuno, and others) started to be applied to polarography. Leaders of this trend were Jaffé [17] and Zuman;[18] the latter applied the Hammett equation to half-wave potentials:

$$\Delta E_{1/2} = E^{X}_{1/2} - E^{H}_{1/2} = \rho\sigma_X,$$

where $E^{x}_{1/2}$ and $E^{H}_{1/2}$ are the half-wave potentials for oxidation or reduction of a compound with a substituent X and an unsubstituted compound, ρ is the reaction constant (measured in volts), σ is the substituent constant. This relationship is valid for both irreversible and reversible electrochemical processes. In the first instance it represents the perturbation introduced by the electronic effect of substituent X to the change in free energy when going from the oxidised (reduced) to the reduced (oxidised) form of the molecule, and in the second instance it represents the perturbation introduced by the substituent to the change in free energy of activation when going from the oxidised (reduced) form to the transitional electrode complex.

It was possible to make use of this concept in order to arrange systematically the material obtained from the polarography of organic compounds and to study the nature of the electronic effect of substituents on the reaction centre (metal atom) in redox reactions.

Comparison of different σ constants of substituents and also from a number of their combinations showed that the best correlation occurs between $E^{o}_{1/2}$ and σ^{0}_{n} derived by Taft.[22] The correlation dependences obtained were successfully used to determine the σ constants of metallocenyl groups and other polyatomic groups.[14,19,27] The electronic effects in ferrocenes,[20,21,23,24,28] and in arenecyclopentadienyliron cations,[29] ruthenocenes and osmocenes[25,30] are such that σ^{0}_{n} constants correlate better with $E_{1/2}$. This indicates that there is conjugation between the aromatic ring and the substituent. However, in *bis*-arenechromium compounds it is very weak, so $E_{1/2}$ for oxidation of *bis*-arene complexes of chromium correlates better with σ_m constants.[26,31,32] The difference between complexes of chromium and other metals is probably due to differences in the nature of the metal−ligand bond,[31] although it should be stressed that in both cases an inductive mechansim for transmission of the electronic effect of substituent to metal atom is the decisive factor.

The half-wave potentials of irreversible processes also correlate with σ constants of substituents. For example, $E_{1/2}$ for the irreversible two-electron oxidation of platinum complexes

$$[P(C_2H_5)_3]_2\,Pt(X{-}C_6H_4)_2 \xrightarrow[-2e]{} [P(C_2H_5)]_2\,Pt(X{-}C_6H_4)_2]^{2+}$$

correlates well with Hammett σ constants,[34] while $E_{1/2}$ for the reduction of chelate complexes of nickel with dithiocations [sic] of general formula $Ni(S_2C_2R_2)_2$ show a linear dependence on the inductive constants of substituents.[35]

It has been shown[36–38] that standard redox potentials E^0 for different one-electron redox transfers in sandwich-type π-complexes of transition metals, such as $Cp_2M^- \rightleftharpoons Cp_2M \rightleftharpoons Cp_2M^+ \rightleftharpoons Cp_2M^{2+}$ give a linear correlation with the corresponding ionisation potentials *IP* of metals and their ions, and this correlation should be common for all metals and all possible redox changes in a series of complexes with the same ligand environment. The existence of such a correlation is due to the fact that the main contribution to the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of metallocenes is made by the atomic orbital (AO) of the metal. Therefore, the potentials for the reactions of metallocenes, including the electron-transfer stage involving the HOMO and LUMO, must be determined by the properties of the metal itself in the given oxidation stage. Although this correlation is approximate and holds for complexes with 12-17 and 19-21 electron configurations (the number of electrons in the valence shell of the metal is given), it is very useful and can be used to predict redox properties from known *IP* values of the metal, and hence also ranges of potential in which different classes of sandwich π-complexes are stable.

In one study[37] a diagram of zones of thermodynamic stability for metallocenes Cp_2M and their cations is given (Fig.1). As can be seen from the diagram, as the atomic weight of M increases the zone of stability for Cp_2M shrinks, in other words, metallocenes of 4d- and 5d-metals are oxidised more readily than their 3d-analogues. This makes it difficult to synthesize heavy metallocenes. The synthesis of doubly charged cations of type $(C_7H_7)M^{2+}$ is also very difficult as they are incompatible with most known solvents as a result of their very strong oxidising capacity ($E^0 > 3.0$ V). Thus, it is very useful to know the values of E^0 when choosing the most convenient method of synthesizing metallocenes and also to understand the nature of the active particles that are formed in reactions catalysed by metallocenes (for example, the products from the

reduction of Cp_2MCl_2, where M = V, Nb, catalyse the low-temperature reduction of carbon monoxide to hydrocarbons in the presence of added quantities of proton-donor compounds[39–41]).

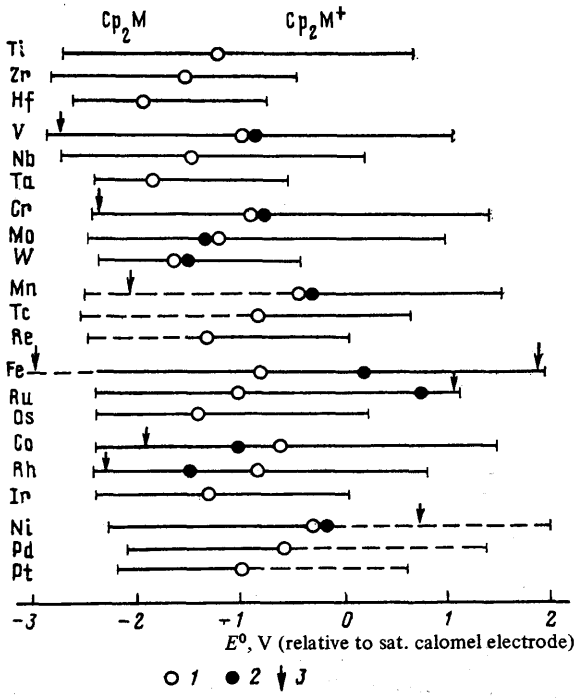


Figure 1. The zones of thermodynamic stability for Cp_2M complexes and their cations; (1) calculated values of E^0 for $Cp_2M^{0/+}$ redox pairs; (2) experimental values of E^0 for $Cp_2M^{0/+}$ redox pairs; (3) experimental values of E^0 for $Cp_2M^{0/-}$ and $Cp_2M^{2+/+}$ redox pairs; the dotted lines denote the zones of stability for Cp_2M^+ cations and Cp_2M complexes for $d^{5/6}$ and $d^{6/7}$ electron transitions for which there is a deviation from the linear dependence of E^0 on *IP*.[37]

Study of π-complexes of Fe, Co, Ni, Cr, Mo, W, Mn, Ru, Re, Au, and Cu,[37,38] has shown that the tangent of the gradient angle of the dependence of E^0 on *IP* for different types of sandwich complexes does not depend on the nature of the ligand and is equal to ~0.11:†

$$E^0 = a + 0.11 \cdot IP,$$

†The tangent of the gradient angle of the correlation dependence must theoretically be close to unity. (Thus, for example in some studies,[42–44] where the correlation between $E_{1/2}$ and *IP* is given for a number of organometallic compounds, it is equal to 0.89, 0.92, 0.98, and 0.87). The experimental value of 0.11 in the relationship obtained in these studies[37,38] is particularly interesting and needs to be explained.

where *a* is a constant dependent only on the nature of the ligand (E_0 in V, *IP* in eV). It has been calculated for the main types of π-ligands: Cp (–2.08 V), C_6H_6 (–0.73 V), $C_7H_7^+$ (+1.52 V), etc.[37]

Studies[42–48] are devoted to linear relationships between $E_{1/2}$ and *IP*. In particular, a correlation has been found between $E_{1/2}$ for the reduction $M^{II} \rightarrow M^{I}$ and the second ionisation potential of Cp_2M metallocenes, where M = V, Cr, Co, Ni.[45] The value of $E_{1/2}$ for the process $Cp_2M^{III} \rightleftharpoons Cp_2M^{II}$ correlates with *IP* for the complexes Cp_2V, Cp_2Cr, Cp_2VCl_2, $CpNi(\eta^3\text{-}C_5H_7)$.[46] The oxidation potentials of bimetallic compounds:

$$R_3M{-}M'R_3 \xrightarrow{-e} R_3M{-}M'R_3^{+\cdot} \rightarrow R_3M^{\cdot} + M'R_3^{+}$$
M, M'=Si, Sn, Ge

correlate with vertical *IP* values.[44]

There is also a linear relationship between the electrochemical potentials for one-electron oxidation and the vertical ionisation potentials for compounds of type R_4Pb.[48]

Thus, it may be concluded from the data examined that in a number of cases the values of $E_{1/2}$, readily measured in solution, can be used to determine ionisation potentials in the gas phase.

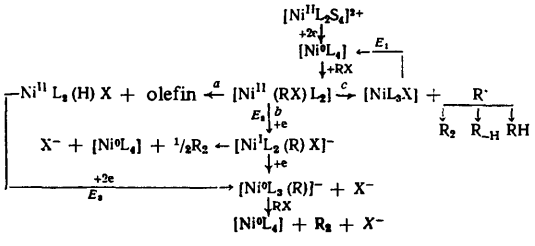
Electrochemical methods can be used to study the disproportionation reactions of unstable complexes of various metals in which the metal is in an intermediate oxidation state and also to determine their HOMO and LUMO energies and spin state.[49] For example, in a study of the two redox systems:

$$Fe^{IV}L_3^+/Fe^{III}L_3 \text{ and } Fe^{III}L_3/Fe^{II}L_3^-$$

it was shown[50] that electrochemical electron-transfer reactions which are accompanied by a change in spin state are slower than reactions in which such a change does not occur. Values of E^0 have also been determined[51] for redox changes of $MF_6^{z/z-1}$ (z = 0, –1, –2; M = Ta, W, Re, Os, Nb, Mo, Ru) and it was shown that for the same metal E^0 increases for the different transitions according to the following series: $d^2/d^3 < d^1/d^2 < d^0/d^1$. The existence of a stepwise relationship between the standard redox potentials and the d^n-configuration of the metal for high-spin and low-spin octahedral complexes has been demonstrated.[52]

Electrochemical methods can be very useful in studying reaction mechanisms. For example, the dimerisation of alkyl and aryl halides catalysed by a Ni(0) complex has been studied.[49] Electrochemical methods were used to show the possibility of regenerating the catalyst, the reaction mechanism was studied and it was established that the Ni(II) complex containing a Ni–R σ-bond that is formed by oxidative addition can decompose by different routes depending on the nature of R (see Scheme 1). Thus, if R = Ar, the complex is thermally stable and can only be broken down by further reduction (route *b*). If R = Alk, the complex is thermally unstable and immediately decomposes according to route *a* (when β-H is present) or route *c*:

Scheme 1



Kochi et al.[48] studied alkyl transfer reactions using lead derivatives as a model and showed that Alk_4Pb reacts with $IrCl_5^{2-}$ according to the scheme:

$$R_4Pb + Ir^{IV}Cl_6^{2-} \xrightarrow{k} R_4Pb^{+} + Ir^{III}Cl_6^{3-}$$
$$R_4Pb^{+} \rightarrow R^{\cdot} + R_3Pb^{+}$$
$$R^{\cdot} + IrCl_6^{2-} \rightarrow RCl + IrCl_5^{2-} \text{ etc.}$$

The linear correlation found between $\log k$ for oxidation of $(C_2H_5)_{4-n}Pb(CH_3)_n$ with hexachloroiridate in acetonitrile and the electrochemical oxidation potentials indicates that the rate-determining stage of the overall process is formation of a radical cation. A similar type of correlation also occurred between $\log k$ in the reaction of Grignard reagents with di-tert-butyl peroxide and $E^{\circ x}_{1/2}$ values of Grignard reagents.[53]

III. REDOX PROCESSES IN WHICH ELECTRON CHANGES ARE LOCALISED ON THE π-BOND ORBITALS

Identification of the general rules governing the change in properties of arenes when coordinated with a metal atom is one of the most important aspects of the chemistry of organometallic compounds. In order to determine this it is possible to make use of an approach based on the comparison of redox properties of free arenes and those coordinated with a metal. Reduction of most complexes and the corresponding uncoordinated ligands in aprotic solvents is a reversible process, which makes it possible to study quantitatively the effect of coordination on the reactivity of π-bonded carbocyclic ligands in redox reactions. A quantitative determination is possible because: 1) these are equilibrium processes, so the difference in reactivity is not due to the nature of the transition state for coordinated and uncoordinated ligands; 2) one-electron reduction processes usually have a low activation energy and proceed rapidly, it may therefore be assumed that the difference between the reduction potentials of coordinated and uncoordinated ligands is caused only by electronic interactions and the changes in steric, solvation, and other effects are minimal; 3) the difference in potentials for reversible reduction of coordinated and uncoordinated ligands determined under the same conditions corresponds to the change in LUMO energies on coordination.

Among the large number of publications devoted to the electrochemical reactions of functional groups of a π-bonded ligand[15] it is possible to select some studies in which attempts have been made to relate the electrochemical behaviour of the compounds with their reactivity and electron properties. For example, a polarographic method was used to determine the electron affinity and σ constants for a number of metallocenyl groups,[54,55] the change in LUMO energy was calculated for acetophenone and benzoquinone when coordinated with $Cr(CO)_3$ [56] and π-$C_5H_5Rh(Ir)$[57] groups respectively. The values of $E_{1/2}$ for oxidation of nitrosyl cation complexes [π-$C_5H_5Mn(NO)LL'$], where L is a Lewis base, can serve as a measure of the π-acceptor properties of Lewis bases as ligands.[58]

The relationship between $E_{1/2}$ and the structure of complexes of Mg, Zn, Cu, Pb, Ni, Co, and V with ethylporphin and other porphyrins has been followed.[59] It was shown that introduction of a metal atom into the porphyrin molecule leads, as a rule, to $E_{1/2}$ changing to a more negative potential, while in a number of complexes of similar structure the change in reduction (oxidation) potentials depending on the nature of the metal is consistent with the change in LUMO (HOMO) energy of the complex.

Coordination affects the reactivity of arenes in different ways depending on the nature and donor-acceptor properties of substituents in the arene.[60,62] Not only the absolute magnitude of the effect can vary here but also its sign. Since the half-wave potential for oxidation of complex to radical cation ($E^{x}_{1/2}$) can serve as a measure of donor-acceptor properties of substituents

$$Arene_2Cr \underset{-e}{\rightleftharpoons} (Arene_aCr)^{+}$$

there must be a connection between the change in $E_{1/2}$ for reduction of arene due to complex-formation ($\Delta E^{ca}_{1/2}$) and $E^{x}_{1/2}$ values. Such a correlation was actually found:[60]

$$\Delta E^{ca}_{1/2} = a + \alpha E^{x}_{1/2},$$
$$a = (0.072 \pm 0.007)\,B;\ \alpha = (0.25 \pm 0.015);$$
$$r = 0.991.$$

Here $\Delta E^{ca}_{1/2}$ is the difference in half-wave potentials between a π-complex with chromium and free arene for a one-electron reversible reduction ($\Delta E^{ca}_{1/2} = E^{c}_{1/2} - E^{a}_{1/2}$).

Thus, the electrochemical cathode reduction reaction is an indicator that can be used to determine the change in free energy on going from arene to π-complex.

The electrochemical reduction of benzalacetophenone and its symmetrical chromium π-complex in DMSO has been studied,[61] and it was shown that the difference in half-wave potential for reduction of π-complex and free arene ($\Delta E^{ca}_{1/2}$) can be regarded as a measure of the effect of coordination on the ability of arene to be reduced to radical anion:

$$\Delta E^{ca}_{1/2} \approx \frac{RT}{nF} \ln \frac{k_c}{k_a}$$

where k_c and k_a are rate constants of reduction for π-complex and free arene respectively.

The dependence of the reactivity of coordinated arene on the nature of the second ligand is a unique feature of *bis*-arenechromium compounds. The high sensitivity of the cathode reaction to substituents in the second ligands is caused by the presence of the chromium atom, which transfers electron density to the ligand, and itself is positively charged.[62] Introduction of a substituent into the ligand has a strong effect on the electron density at the chromium atom and on the dative component of the metal–ligand bond, therefore for these components $\rho = 0.51$ V [62] (we should mention for comparison that $\rho = 0.33$ V [18] for the cathode reduction of substituted benzaldehydes in aqueous alkaline solution).

Thus, the electronic effects of substituents are transmitted from one ligand to another, and the chromium atom considerably intensifies the substituent effect on the second ligand, in other words, the systems in their way resemble an "amplifier" in radioelectronics. The half-wave potential for oxidation of *bis*-arenechromium ($E^{x}_{1/2}$) can be used as an indicator of the capacity of the chromium atom to transmit electron density to ligands. As was also demonstrated,[60] there is a linear correlation between $E^{x}_{1/2}$ and the change in reactivity in the cathode reaction when going from free arene to chromium π-complex ($\Delta E^{ca}_{1/2}$). The correlation equation obtained can be reduced to the general form:[62]

$$\Delta E^{ca}_{1/2} = b + \beta \sum \sigma,$$

where $b \approx 0.125$ V, $\beta = 0.13$ V. It follows from this that the first term in the equation is constant and is independent of the nature of substituent, while the second term expresses the effect of substituent

on the change in free energy when going from free arene to π-complex. The larger the electron-withdrawing effect of the substituent the greater is the decrease in absolute value of $\Delta E^{ca}_{1/2}$.

IV. REDOX PROCESSES IN WHICH ELECTRONIC CHANGES ARE LOCALISED ON THE σ-BOND ORBITALS

The reduction or oxidation of compounds with an M—M, M—C, or M—Hal σ-bond is known to be an irreversible process in most cases. In order to achieve a correlation between $E_{1/2}$ and the structural features, an essential condition is that there exists a constant electron-transfer coefficient for a series of compounds of similar structure. Experimental data indicates that when π-complexes contain localised σ-bonds, reduction in most cases affects only that bond which has the LUMO as an antibonding orbital. Capture of an electron in this orbital leads to cleavage of the σ-bond. When homo- and hetero-polymetallic compounds containing an M—M σ-bond are reduced, metal carbonyl anions $[L_nM]^-$ are usually formed, and readily undergo electrochemical oxidation.[64,65] There is a linear correlation between $E_{1/2}$ for oxidation of anion to radical and $\log k_2$, where k_2 is the rate constant for the nucleophilic substitution reaction:

$$[L_nM]^- + RHal \xrightarrow{k_2} L_nMR + Hal^-.$$

By comparing the values of k_2 for different anions it is possible to determine their relative nucleophilicity, and on the basis of the correlation obtained the relative nucleophilicity of those anions for which direct measurements of k_2 are not possible can be predicted. Using the experimental data obtained for various metal-containing anions (M = Bi, Sb, As, Ge, Sn, Pb, Fe, Ru, Co, Ni, Mn, Re, Cr, Mo, W) as a basis, the following conclusions have been made: in Groups Va, VI, and VII the nucleophilicity of the anions increases on moving down the Group, while in Groups VIII and IVa the nucleophilicity increases going up the Group.[65]

Extension of this approach showed that after measuring the oxidation and reduction potentials of two organometallic compounds it is possible to predict whether a one-electron exchange reaction will take place between them.[66] Thus, for example, for the reaction

$$m^- + S \rightarrow m^{\cdot} + S^- \qquad (1)$$

(where m^- is a metal-containing anion and S is a neutral or charged electron-acceptor molecule) a table has been compiled,[66] in which metal-containing anions arranged in order of increasing nucleophilicity (decrease in $E^{ox}_{1/2}$) are aligned vertically, while acceptor molecules, namely, different organometallic compounds which have $E^{Red}_{1/2}$ values that decrease in absolute value from left to right, are aligned horizontally. So in the top right-hand corner of the table are entered rapid reactions, while in the bottom left-hand corner are reactions which do not go at all or occur extremely slowly. And although the oxidation of anions to radicals on mercury or platinum electrodes is irreversible and $E_{1/2}$ is a kinetic rather than a thermodynamic parameter, the predictions based on these data are in good agreement with experiment (see Table.1).

Polarographic reduction of compounds of type $[\pi\text{-}C_5H_5M(CO)_3]_2$ and $\pi\text{-}C_5H_5M(CO)_3X$ (where M = Cr, Mo, W; X = Hal, CN, Ar, Alk) has been studied[67] and it has been shown that the ease of reduction of the M—M σ-bond decreases on changing from Cr to W.

Studies on the reduction of metal complexes that contain metal-halogen σ-bonds have shown[15,67] that the order of decrease in ease of reduction of this σ-bond for both one-electron and two-electron reduction is opposite to the series of increasing electronegativity of the halogens Cl > Br > I that determines the polarity of this bond. The observed order for decrease in ease of reduction of the M—Hal bond agrees with that of the change in $E_{1/2}$ values for reduction of the C—Hal bond in alkyl halides, which is accounted for by a radical mechanism for reduction. It may be concluded from this that the M—Hal bond in carbonyl complexes of transition metals has a strongly covalent character and has a tendency mainly to homolytic cleavage and not heterolytic cleavage.

Table 1. The dependence of the rate of reaction of (1) on $E^{ox}_{1/2}$ and $E^{Red}_{1/2}$ of reagents (DME, Ag/AgCl).[66]

Metal-containing anion ($E^{ox}_{1/2}$, V)	Acceptor molecules ($E^{Red}_{1/2}$, V)								
	$Cr(acac)_3$ (−2.5)	azulene (−2.3)	(bipy). $Mo(CO)_4$ (−2.2)	$Fe(acac)_3$ (−1.4)	1,3,5-trinitrobenzene (−1.3)	$Co(acac)_3$ (−1.2)	$(C_6H_6)_2Cr^+$ (−1.2)	quinone (−1.2)	$Mn(acac)_3$ (−0.8)
Ph_2Sb	*f*	—	—	—	—	—	—	*f*	—
Ph_3Ge	*f*	*	*s*	*f*	*f*	*f*	*f*	*f*	*f*
Ph_2Sn (−1.9)	*s*	*s*	*s*	*f*	*f*	*	*f*	*f*	*f*
$CpFe(CO)_2$ (−1.9)	*s*	*s*	*s*	*f*	*f*	*f*	*f*	*f*	*f*
PhSe (−1.6)	—	—	—	*f*	—	*s*	—	*f*	*f*
PhS (−1.4)	—	—	—	*s*	—	*s*	*s*	*s*	*f*
Ph_3Pb (−1.4)	—	—	—	*s*	*f*	*s*	*s*	*f*	*f*
$Cp_2Mo(CO)_3$ (−1.1)	—	—	—	*f*	*s*	*s*	*f*	*f*	*f*
$CpCr(CO)_3$ (−1.1)	—	—	—	—	*s*	—	—	*f*	*f*

Notation: *f*—fast; *s*—slow.

*Time for half-conversion was 4 sec.

Transition metal compounds with a metal—carbon σ-bond are reduced, as a rule, at more negative potentials than complexes with M—Hal and M—M σ-bonds, and this occurs in a single irreversible stage that involves addition of one or two electrons. The irreversibility of the waves is due to the high reactivity of the particles formed. Three possible types of transition state in the reduction of the Fe—R bond for a series of $\pi\text{-}C_5H_5(CO)_2FeR$ compounds have been examined.[74] The route that leads to polarisation of the form $(Fe^{\delta+}\cdots R^{\delta-})$ can immediately be rejected as the least favourable, and the choice between radical $(Fe^{\cdot}\cdots R^{\cdot})$ and ionic $(Fe^{\delta-}\cdots R^{\delta+})$ routes can be made by studying the effect of substituents at the *para* position of the σ-phenyl ring on reduction. A linear correlation occurs between $E^{Red}_{1/2}$ and σ^0_n ($r = 0.973$, $\rho = 0.12$ V). If the contribution of the conjugation effect is greater than that allowed by σ^0_n, then large deviations from a linear relationship occur for such substituents. This fact and also the low value of ρ suggest that in the transition state of the electrochemical reaction studied the demands of the "reaction centre" for a polar substituent effect are not large, which corresponds well with a proposed homolytic type of activation of the Fe—C bond in the electrode field.

It has been shown[68] that replacement of a CO group in $\pi\text{-}C_5H_5.Re(CO)_3$ compounds by a phosphine ligand leads to a change in reduction mechanism (one-electron rather than two-electron). The values of $E_{1/2}$ of the first reduction wave were used to determine the

effect of substituents on the transition state of the electrode reaction. The best linear correlation occurred between $E_{1/2}^{Red}$ and the sum of the inductive constants from substituents at the phosphorus atom or with the basicity of the corresponding phosphines.

The polarographic reduction of compounds of type $XM(CO)_5$ (M = Mn, Re; X = Hal, Ar, acetyl, aroyl) occurs irreversibly according to a two-electron mechanism.[69] In all cases there is homolytic activation of the bond being reduced. In contrast to other types of σ-bond, the reduction of the M–C σ-bond (aromatic ring) is virtually independent of the nature of the metal.[69] The effect of substituents in the benzene ring of aryl derivatives on $E_{1/2}^{Red}$ is also small, which suggests that there is no conjugation between the aryl group and the metal atom in both the ground and transition states. However, the $E_{1/2}^{Red}$ values of acyl substituents vary considerably with the nature of the substituent. A good linear relationship is observed between $E_{1/2}^{Red}$ and Hammett σ constants (r = 0.985); ρ = +0.288 V and is the same for both Re and Mn derivatives.

An investigation using polarography and cyclic voltammetry showed[70] that reduction of planar cobalt chelate complexes occurs in the following way (chel is polydentate chelate ligand):

$$[RCo^{III}(Chel)L] \underset{-e}{\overset{+e}{\rightleftharpoons}} [RCo^{III}(Chel)L]^- \underset{-e}{\overset{+e}{\rightleftharpoons}} [RCo(Chel)L]^{2-}.$$

The $E_{1/2}$ values of the first reduction stage for the same type of complex depend on R, in other words, the electron affinity of the organometallic chelate depends on the stability of the R^- anion, and there is a correlation between $E_{1/2}^{Red}$ and pK_a (RH). This means that the orbital into which the electron goes on reduction is the antibonding orbital of the Co–C bond. Thus, the electrode process examined can serve as a model of a reductive cleavage reaction.

It was previously shown[71] that there is a clear correlation between the nucleophilicity of Co(I) complexes in oxidative addition reactions and $E_{1/2}$ for reduction of complexes Co(II) → Co(I). Special attention should be given to the fact that redox potentials of cobalt chelates can vary over a very wide range depending on the nature of the ligand. If the electron density on the Co atom varies to the same extent, the distribution of charge on the Co–C bond must vary accordingly. A change in electron density on the Co atom and a distribution of charge on the Co–C bond can mean that there are various mechanisms for cleavage of this bond, including the extreme cases – nucleophilic and electrophilic and electrophilic reactions on the carbon atom—and the intermediate homolytic cleavage. Such an approach can possibly be used to develop the chemistry of coenzymes that belong to the vitamin B_{12} group and which contain a Co–C bond.

Polarography can be a convenient method for determining the electron affinity of various radicals.[72,73] Organomercury compounds that are reduced on an Hg cathode in two one-electron stages can be used for this purpose:

$$RHgHal + e \rightarrow RHg^{\cdot} + Hal^-,$$
$$RHg^{\cdot} + e \xrightarrow{H^+} RH + Hg.$$

Since the C-Hg bond in $RHg^{\cdot}$ is weakened, it may be assumed that when this particle is reduced the changes in electron density are localised mainly in the half-filled orbital of R$^{\cdot}$, so that there is a good linear correlation between $E_{1/2}$ for the second reduction wave and the electron affinity of radical R$^{\cdot}$. The limited number of other methods for determining this value are less accurate. Study of the dependence of $E_{1/2}$ for the second wave on the substituent in the radical showed[73] that the best correlation occurs between $E_{1/2}^{Red}$ and σ_n^0, namely, the dependence of $E_{1/2}^{Red}$ on polar effects is small, as is typical for homolytic cleavage of a bond.

Electrochemical data can be used to predict the type of decomposition of radical cations formed as intermediates. Decomposition of the form $RH^{+\cdot} \rightarrow R^{\cdot} + H^+$. The scheme for decomposition of the triethylsilane radical cation predicted[74] on the basis of this principle

$$(C_2H_5)_3SiH \underset{-e}{\rightarrow} [(C_2H_5)_3SiH]^{+\cdot} \rightarrow (C_2H_5)_3Si^+ + H^{\cdot}$$

($E_{1/2}^{ox}$ = 0.230 V) is in good agreement with the experimental data.

Electrochemical methods can be successfully used to study the properties of organomagnesium compounds, in particular for determining their basicity.[75] Cathode-anode polarisation curves of solutions of RMgX and R_2Mg in THF on a hydrogen electrode probably correspond to the following process:

$$RMgX + {}^1/_2H_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} RH + MgX^+.$$

The zero current potential $E_{i=0}$ of the polarisation curve is the equilibrium value for this redox system and depends on the basicity of RMgX. The pH value [sic] of solutions of organomagnesium compounds, calculated as a function of $E_{i=0}$, is a quantitative measure of their basicity. Polarography data can be used to determine the acidity of hydrocarbons. Determination of the acidity of weak CH acids such as hydrocarbons is not possible by a direct method because of the large pK_a value for most hydrocarbons and their slow dissociation. At the same time it is possible to measure the equilibrium constants of other reactions of carbanions and compare them with the pK_a values of hydrocarbons. The first attempt to use polarography for determination of the relative stability of carbanions was undertaken by Streitwieser and Perrin,[76] who tried to relate $E_{1/2}^{Red}$ for substituted benzyl chlorides and polycyclic arylmethyl chlorides in DMF with pK_a values of the corresponding arylmethanes. Then the $E_{1/2}$ value of the second reduction wave of organomercury salts was suggested[77] as a measure of the relative acidity of CH acids. However, the use of this parameter did not prove very successful because the value of $E_{1/2}^{Red}$ for the second wave depends on the rate of dimerisation of the initially formed radicals. A correlation was found successfully in two studies,[78,79] in which it was recorded that the acidity of CH acids over a wide range of pK_a values is related to the polarographic reduction parameters for symmetrical organomercury compounds R_2Hg, which undergo a two-electron reduction to form the corresponding carbanions R^-. There was found to be a linear relationship between values of $\alpha n_\alpha E_{1/2}$ (α is the electrochemical transfer coefficient, n_α is the number of electrons in the potential-determining stage) and pK_a values:

$$\Delta(\alpha n_\alpha E_{1/2}) = \rho \Delta pK_a,$$

where ρ is an empirical coefficient that is dependent on the experimental conditions. Using this equation a scale of CH acidity covering more than 50 hydrocarbons was compiled. Later the CH

acidity of some brominated toluenes was determined by the same method.[80]

Denisovich and Gubin[81] studied three series of compounds—RHgX, R_2Hg, and σ-derivatives of π-cyclopentadienyldicarbonyliron—in order to compare the reduction parameters and pK_a (RH). All these compounds are reduced by cleavage of the carbo–metal bond to give the carbanion R^-. The correlation between $E_{1/2}$ and structure is known to be good only for reversible processes. For irreversible processes the correlation holds only if the α coefficient is strictly constant. The reason for the scatter in α values for the different series of organomercury compounds is related to the unsaturated state of the coordinated mercury atom, which leads to complex-formation between molecules of organomercury compound and solvent and with each other. Iron π-complexes are free of these problems. The α coefficient for these series is virtually constant. It is therefore more suitable to use σ-derivatives of π-cyclopentadienyldicarbonyliron in the determination of unknown pK_a (RH) values. It is true that a significant shortcoming of these compounds is that it is difficult to synthesize them. The pK_a values of ferrocene have been determined[81] as well as those of cyclopentadienyltricarbonyls of manganese and rhenium.

Up to this point we have examined studies in which electrochemical methods have been used on processes that occur with cleavage of a carbon– metal σ-bond and on the properties of the particles formed by this. However, it is also possible to use electrochemical methods to determine the tendency of compounds to form such a bond. For example, it was shown[82] that preliminary polarographic analysis can be a useful test of whether benzyl bromide containing different substituents in the ring will readily undergo a reaction with metallic mercury to give the corresponding benzylmercury bromide. The C–Br bond in benzyl bromide is known to be reduced in a single two-electron stage (see [3], p.217). Such behaviour was observed[82] for unsubstituted benzyl bromide, the three isomeric monobromo derivatives, 3,5-dibromo- and pentafluoro-benzyl bromides. However, pentabromo-, pentachloro-, 2,3,4,6-tetrabromo-, 2,4,6-tribromo-, and 2,6-dibromo-benzyl bromides give polarograms that are identical with those of the corresponding benzylmercury bromides. This suggests that these benzyl bromides are reduced via organomercury compounds that are rapidly formed by contact of the benzyl bromides with the surface of the mercury electrode. Reduction by this route in fact occurs for those benzyl bromides which give organomercury compounds after a short time in good yield when the reactions are carried out preparatively.

Electrochemical methods in combination with different spectral methods can provide valuable information on the electronic structure of σ- and π-organometallic compounds, the charge transfer mechanism in reduction or oxidation products, the distribution of spin density in molecules, and skeletal rearrangements during reduction or oxidation. Answers to these questions are important for both theoretical and preparative chemistry. For example, there are a number of studies[83–89] on the mechanism for charge transfer to the metal atom and carbonyl groups in octahedral and bipyramidal complexes of Fe, Cr, Mo, and W and in their one-electron reduction products. It was shown that in the octahedral complexes transfer of charge to and from the metal atom occurs by a σ-mechanism, namely, one involving metal–ligand σ-bonds, while in the bipyramidal complexes there is a π-mechanism for charge transfer towards the metal atom, namely, one involving metal–ligand π- or δ-bonds, and a σ-mechanism in the opposite direction. The force constants calculated from IR spectra for octahedral complexes of the form $LM(CO)_5$ (M = Cr, Mo, W; L = Py, quinoline) and their reduction products are also discussed in terms of σ- and π-bonding; the electrochemical properties and EPR spectra of 27 different bimetallic compounds were also studied.

V. SIMULTANEOUS CALCULATION OF ELECTROCHEMICAL OXIDATION AND REDUCTION POTENTIALS OF ORGANOMETALLIC COMPOUNDS IN ORDER TO DETERMINE THEIR REACTIVITY

In the studies examined in the preceding chapters, the relation between the reactivity of a compound and only one of the redox potentials–oxidation potential or reduction potential—has been investigated. In our opinion a much more fundamental relation between the electrochemical potentials and electronic structure of molecules and their reactivity can be followed if both the oxidation potentials and reduction potentials measured under the same conditions are known. Then for reversible electrochemical processes it is possible to determine the relative energies of frontier HOMO and LUMO orbitals, their change of position in relation to molecular structure, and also the magnitude of the energy gap between these orbitals, on which the stability of a molecule is dependent during thermal or photoexcitation. In the case of irreversibly oxidised or reduced systems, which includes the majority of organic compounds, similar direct correlations are less good. Nevertheless, it may transpire that even for electrochemically irreversible processes the effect of substituents in a series of related substrates on $E_{1/2}^{ox}$ and $E_{1/2}^{Red}$ will have a corresponding effect on the HOMO and LUMO energies, and then readily available electrochemical potentials can be used to predict reactivity at a semi-quantitative level.

Such an approach was used for the first time[90] when oxidation and reduction potentials on a platinum electrode under absolutely identical conditions were measured for 35 alkyl-, aryl-, and benzylmercury halides. On the basis of the derived values of the half-wave potentials for oxidation and reduction, a new classification of organomercury halides was proposed, making it possible to predict their relative reactivity in reactions with different forms of cleavage of the C–Hg bond (Fig.2, Table 2). According to this classification organomercury compounds can be divided into four types—anionogenic, cationogenic, radicalogenic, and inert (labelled as A, C, R, and I respectively in Fig.2); this reflects the relative stability of carbanions (A), carbocations (C), and radicals (R) formed. This classification is very provisional and there is no sharp boundary between groups. For example, not only secondary benzyl but also primary benzyl and alkyl organomercury compounds can undergo radical decomposition. It should however be emphasised that on moving upwards along the diagonal *ir* the relative tendency to radical decomposition will increase, since as this occurs the magnitude of "the inherent polarographic gap" of the compound (i.e, the difference $E_{1/2}^{ox} - E_{1/2}^{Red}$) will decrease.

In one study,[91] of the stability of organometallic compounds (OMC) in their synthesis and decomposition processes, the values of the OMC ionisation potentials (or oxidation potentials in solution) are used to predict the stability of the compounds and their tendency to different types of cleavage of the C–M bond. For nontransition metals that have ionisation potentials IP_M of the order of 4–8 eV, there is typically formation of those OMC for which $IP_{OMC} > IP_M$ (when $IP_R > IP_M$) with organic radicals ($IP_R \sim 8-10$ eV). In this

case as a result of the electropositive nature of the metal the contribution of the orbital of the radical to the HOMO in the organometallic compound will be greater, which corresponds to the formation of a polar M–R bond with a negative charge on R. When $IP_M \approx IP_R$ the M–R bond will be covalent, even though $IP_{OMC} > IP_M \approx IP_R$. When $IP_M > IP_R$ the negative charge of the dipole will be localised on the metal atom and the HOMO will have a primary contribution from the metal orbital.

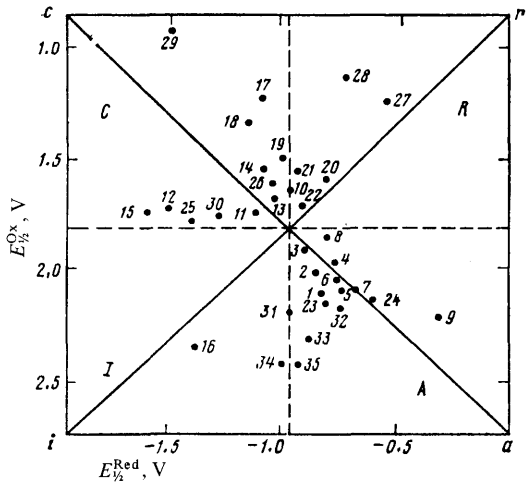


Figure 2. The classification of RHgHal compounds in accordance with their oxidation and reduction potentials measured on a Pt electrode in CH_3CN with 0.05 M Bu_4NBF_4 as supporting electrolyte at 20 °C relative to Ag/AgCl (sat. KCl), ω = 2700 revs/min.[90] Organomercury compounds of type 4-X–$C_6H_4CH(COOEt)HgHal$ (points 1–9) where X is: (1) tert-C_4H_9, (2) iso-C_3H_7, (3) C_2H_5, (4) H, (5) F, (6) Cl, (7) Br, (8) I, (9) NO_2; organomercury compounds of type AlkHgHal (points 10–16) where Alk is: (10) C_2H_5, (11) n-C_3H_7, (12) n-C_4H_9, (13) iso-C_3H_7, (14) tert-C_4H_9, (15) neo-C_5H_{11}, (16) CF_3; organomercury compounds of type Y–$C_6H_4CH_2HgHal$ (points 17–26) when Y is: (17) 4-OCH_3, (18) 4-CH_3, (19) 4-H, (20) 4-F, (21) 4-Cl, (22) 4-Br, (23) 4-CF_3, (24) 4-NO_2, (25) 3-OCH_3, (26) 3-Br; organomercury compounds of type $ArCH(CH_3)HgHal$ (points 27 and 28) where Ar is: (27) C_6H_5, (28) 8-quinoly; organomercury compounds of type 4-Z–C_6H_4HgHal (points 29–35) where Z is: (29) $N(CH_3)_2$, (30) OCH_3, (31) iso-C_3H_7, (32) CH_3, (33) H, (34) F, (35) Br.

However, calculation of only the ionisation potentials (or oxidation potentials in solution) is insufficient for an understanding of the nature of the R–M bond, since, as mentioned above, there is no one-to-one correspondence between the values for oxidation and reduction potentials. Simultaneous calculation of the tendency of OMC to both oxidation and reduction makes it possible in many cases to rule out a structure of type $R^+ - M^-$. These are probable only for compounds that are readily oxidised and are difficult to reduce, but if the compounds that are readily oxidised are comparatively easy to reduce, then a nonpolar structure R–M should be considered instead of structure $R^+ - M^-$. This is in accordance with the suggestion[90] that readily oxidised and reduced compounds must have a tendency to decompose into radicals.

Table 2. The classification of organomercury halides RHgHal on the basis of their electrochemical potentials.[90]

Area in Fig.2	RHgHal		R	Typical reactions
	oxidised	reduced		
C (cationogenic)	readily	with difficulty	ZC_6H_4, Alk, $ArCH_2$	$RHgHal \overset{+e}{\rightleftarrows} (RHgHal)^{\cdot-}$ $RHg^+ \rightarrow R^\cdot + Hg$
A (anionogenic)	with difficulty	readily	ArCH(COOEt), $4\text{-}NO_2C_6H_4CH_2$, YC_6H_4	$RHgHal \overset{+e}{\rightleftarrows} (RHgHal)^{\cdot-}$ $RHgHal + N^- \rightarrow R^- + HgHalN$
R (radicalogenic)	readily	readily	ArCH (Alk)	$RHgHal \rightarrow R^\cdot + HgHal^\cdot$ $RHgHal \overset{+e}{\rightleftarrows} (RHgNal)^{\cdot-} \rightarrow R^\cdot + Hg + Hal^-$ or $RHgHal \overset{+e}{\rightleftarrows} (RHgHal)^{\cdot-} \rightarrow R^\cdot + HgHal^-$
I (inert)	with difficulty	with difficulty	CF_3, R_F	—

Notation: Z—strong electron-donor; Y—strong electron-acceptor, N—mercurophile.

The approach suggested in this work[90] is also very fruitful for studying bimolecular reactions. It has been used[92] to study symmetrization reactions of substituted ethyl α-bromomercuryphenylacetates. Since the substituent effect conforms to the Hammett equation both in symmetrization[93] and (with a poorer correlation coefficient) electrochemical reduction of ethyl α-bromomercuryphenylacetates,[33] there must automatically be a correlation between $\log k_{symm}$ and $E^{Red}_{1/2}$. However, it does not follow from this that both reactions have an identical or similar mechanism (for example, symmetrization occurs via one-electron transfer) as the Hammett equation is obeyed by hundreds of reactions with a variety of mechanisms. The conclusion[33] that the rate of symmetrization tends to increase as the tendency of RHgHal to reduction grows but is not related in any way to its tendency to oxidation, is not at all consistent with a cyclic structure for the transition state in which one of the two RHgHal molecules is a donor and the other an acceptor. Therefore, in establishing correlations between redox potentials and rates of reaction it would be necessary to seek approaches in which both $E^{Red}_{1/2}$ and $E^{Ox}_{1/2}$ were taken into consideration.

An equation was obtained[92] for the symmetrization reaction, relating the rate of symmetrization to the electrochemical oxidation and reduction potentials of organomercury halides:

$$\log k = a(1/G_1 + 1/G_2) + b, \qquad (2)$$

where *a* and *b* are constants, $G_1 = E^{Ox}_{1/2} - E^{Red}_{1/2}$ is the polarographic gap for the given RHgX, $G_2 = E^{Ox}_{1/2}(Hg-Br) - E^{Red}_{1/2}$ is the difference between the oxidation potential of the Hg–X bond (when X = Br) and $E^{Red}_{1/2}$ (see Fig.3). It follows from this that organomercury salts that are readily oxidised and readily reduced must also readily undergo symmetrization, namely, an increase in electron-withdrawing properties of the substituents in the benzene ring must have an

accelerating effect, which was in fact observed experimentally.[93] This is due to the increased degree of nucleophilic assistance exerted by the bromine atom in the RHgBr molecule, but at the same time the ability of the R–Hg σ-bond in the other molecule to coordinate with the mercury atom of the first molecule must also increase. The second effect is stronger in all cases, namely, the decisive factor is dependence on the inherent polarographic gap. For a cross-symmetrization reaction the regioselectivity of reaction was shown[92] to be related to the electrochemical parameters of the reagents.

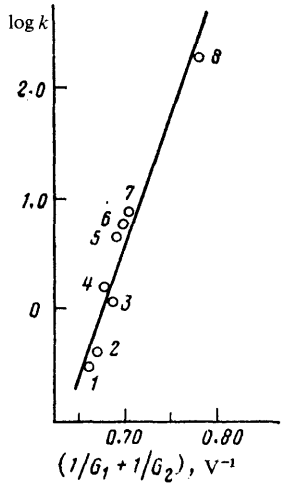
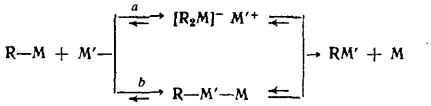


Figure 3. The dependence of the logarithm of rate constant for the symmetrization reaction of 4-X–$C_6H_4CH(COOC_2H_5)HgBr$ on the magnitude of the polarographic gap[92] where X is: (1) tert-C_4H_9, (2) iso-C_3H_7, (3) C_2H_5, (4) H, (5) F, (6) Cl, (7) Br, (8) I, (9) NO_2.

An electrochemical method has been used[94] to study the bromo- and iodo-mercuration of organomercury halides and an equation similar to (2) has been selected, only in this case $G_1 = E^{o}_{1/2}(\text{RHg}.\text{.Hal}) - E^{\text{Red}}_{1/2}(\text{Hal}_3^-)$; $G_2 = E^{o}_{1/2}(\text{Hal}_3^-) - E^{\text{Red}}_{1/2}(\text{RHgHal})$. The results obtained[94] can briefly be summarised as follows: 1) if RHgX is readily oxidised and readily reduced, the reaction must proceed rapidly since both electrochemical gaps G_1 and G_2 will be narrow; 2) if RHgX is readily oxidised but is reduced with difficulty, the rate of reaction is mainly determined by gap G_1 and will be higher the narrower this gap; 3) if RHgX is readily reduced but oxidised with difficulty, the rate of reaction is mainly determined by gap G_2 and will be higher the narrower this gap; 4) if RHgX is oxidised with difficulty and reduced with difficulty, the reaction must proceed slowly as both gaps will be wide. These conclusions are valid not only for bromomercuration but also apparently for other reactions of organomercury compounds that proceed via a cyclic transition state. The important factor is the relative position on the potential scale of the oxidation and reduction levels of the second ("electrophilic") agent, the width of gaps G_1 and G_2 being dependent on this.

An attempt was made[95] to predict the reaction pathway–ionic (a) or covalent (b)—for redox transmetallation reactions:



On the basis of the redox properties of the reacting metals (metal complexes or metalloids) expressed numerically as ionisation potential (*IP*) and electron affinity (*E*)‡ it was concluded that in reactions involving two metals M and M′, each of which has $IP + E < 8$ eV, ionic compounds are formed as intermediates. When $IP + E >$ 10 eV, covalent bonding occurs. Metals, metalloids, and complexes that have an average total value of $IP + E$ in the region 8–10 eV can evidently react by either an ionic or covalent pathway depending on the conditions. These findings make it possible to carry out a purposeful synthesis of polynuclear compounds and to choose metals–catalysts in thermodestruction processes of organometallic compounds.

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From the material reviewed it may be concluded that electrochemical redox potentials can be used as energy characteristics of reagents in order to analyse the effect of structure on reactivity. A rational approach is to assign oxidation and reduction potentials to specific localised sites of electron change in the molecule being studied (bonds, individual atoms) during electrochemical oxidation and reduction and then to local regions of change in electron density in a nonelectrochemical reaction.

In order to establish a correlation between the rates of homogeneous reactions and electrochemical potentials it is necessary to measure both the oxidation potential and the reduction potential of both reagents. With such an approach it is possible to reveal the essential features of the reaction, which cannot be detected when a correlation with only $E^{o}_{1/2}$ or only $E^{\text{Red}}_{1/2}$ is considered; an example of this is the degree of reaction compatability on the terminal atoms of reacting molecular fragments (relative contribution of G_1 and G_2).

It cannot be concluded from the existence of a correlation between the rates of reaction and electrochemical potentials that these reactions must proceed according to a one-electron transfer mechanism (similarly for the existence of correlations with ionisation potentials or electron affinity) since both the rate of reaction and the redox potentials are related to the energies of the frontier orbitals. Interaction between the frontier orbitals does not necessarily lead to complete electron transfer and the formation of radical cation and radical anion particles.

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‡Instead of these properties the possibility of using the values of the standard redox potentials of reagents is admitted by Bochkarev and Pankratov.[95]

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Polymers Based on Unsaturated Derivatives of Carbaboranes

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The literature data on the polymerisation and copolymerisation of unsaturated derivatives of carbaboranes and silicon- and carbaborane-containing compounds as well as the physicochemical properties of the polymers obtained are surveyed. Special attention has been devoted to the synthesis of polymers with dicarbaundecaborate fragments and metallocarbaborane complexes based on them.
The bibliography includes 118 references.

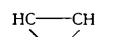
CONTENTS

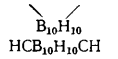
I. Introduction 875
II. Carbochain polymers based on unsaturated derivatives of carbaborane(12). 875
III. Silicon-carbaborane-containing polymers 879
IV. Polymers containing dicarbaundecaborate fragments 880

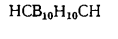
I. INTRODUCTION

One of the interesting advances in the modern chemistry of organoelemental compounds is the discovery in 1962–1963 of carbaborane(12)† $C_2B_{10}H_{12}$ and its derivatives—a new class of electron-deficient polyhedral systems.[1-3] The great synthetic possibilities due to the high reactivity of the B–H and C–H bonds in the carbaborane nucleus and the unusual thermal behaviour of carbaboranes[4,5] have attracted the attention of investigators to these boron compounds for more than 20 years.

Carbaborane(12) has three isomeric forms which have come to be represented schematically in the following manner:[6]


1,2-dicarba-*closo*-dodecaborane(12) (*o*-carbaborane)


1,7-dicarba-*closo*-dodecaborane(12) (*m*-carbaborane)


1,12-dicarba-*closo*-dodecaborane(12) (*p*-carbaborane)

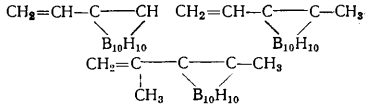
A large series of compounds have been synthesised on the basis of carbaboranes,[6-11] many of which are used to obtain various classes of polymers containing carbaborane units in the main or side chain. Carbaborane-containing polymers are obtained both by polymerisation and polycondensation methods. The advances in the synthesis of these polymers have been examined in a series of monograph and reviews,[12-18] but the latter have been devoted mainly to polymers of the polycondensation type. Hitherto there have been virtually no reviews on the polymerisation and copolymerisation of unsaturated carbaborane-containing monomers and to the study of the properties of carbochain polymers based on them. Nevertheless, appreciable progress has been noted in this field in recent years. The copolymerisation of carbaborane-containing compounds with vinyl monomers, which makes it possible to impart new valuable properties to known polymers by introducing carbaborane nuclei into their structure which as a rule increases the temperature of the onset of the decomposition of the polymers and the yield of the coke residue, has aroused special interest.

Since 1984, information has appeared in the literature on the polymerisation of new types of monomers—unsaturated derivatives of dicarbaundecaborates. A special section of the review has therefore been devoted to polymers with dicarbaundecaborate fragments and to polymeric metallocarbaborane complexes based on them.

II. CARBOCHAIN POLYMERS BASED ON UNSATURATED DERIVATIVES OF CARBABORANE(12)

The problem of the synthesis of polymerisation carbaborane-containing polymers reduces to a study of the reactivity of the monomer, which is also usual for other compounds, and the allowance for specific properties of icosahedral carbaboranes such as the presence of steric hindrance due to bulky groups and the electron-accepting character of the carbaborane nucleus, which reduces the electron density in the double bonds of alkenylcarbaboranes.[13] In addition, one should note the sensitivity of the carbaborane groups to the action of the nucleophiles.[19] For this reason, the attempts to carry out the radical and ionic polymerisation of alkenylcarbaboranes were unsuccessful for a long time or led only to the formation of oligomers.

The first carbaborane-containing carbochain polymers were synthesised by polymerising monomers containing the vinyl group linked directly to the carbon atom of the *o*-carbaborane nucleus:



The polymerisation was carried out in solution or in bulk in the presence of phenyl-lithium at 33–200 °C. This yielded polymers with a molecular weight of $(1.4-7.1) \times 10^4$, which have been proposed as a component of the solid fuel for rocket engines.[20]

Subsequently, polyvinyl-*o*-carbaborane with a molecular weight (MW) ranging from 5×10^4 to 14×10^4 was obtained at room temperature in solution in ethyl ether in the presence of phenyl-lithium.[21] The polymers were white amorphous substances with a softening temperature of 250–280 °C (depending on the MW), soluble in benzene and ether, and insoluble in aliphatic hydrocarbons. The radiation-induced polymerisation of vinyl- and isopropenyl-*o*-carbaboranes in the melt at 100–140 °C [22] also leads to the formation of soluble polymers with MW up to 2.5×10^4.

† Dicarbadodecaborane(12) (Ed. of Translation)

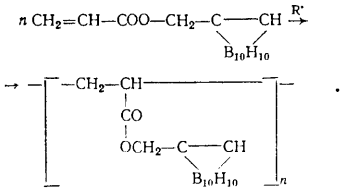
The polyvinyl-*o*-carbaborane synthesised by polymerising vinyl-*o*-carbaborane at 31 °C under the influence of γ-radiation[23–25] differs in its properties from those described above. It does not soften up to 430 °C, is readily soluble in alcohols, acetone, and dimethyl sulphoxide, and is less soluble in hexane and benzene. It has been found that the yield of the polymer increases linearly with increase in the radiation dose, reaching 50% for a dose of 3.5×10^{21} eV g^{-1} h^{-1}. The rate of polymerisation is proportional to the intensity of radiation raised to the power 0.76, the maximum degree of polymerisation being 11–12. The set of IR and ^1H and ^{11}B NMR spectroscopic data justified the hypothesis that the polymerisation of vinyl-*o*-carbaborane under the influence of γ-radiation is of the "head to tail" type.

All the attempts to obtain a polymer from isopropenyl-*o*-carbaborane by radical polymerisation were unsuccessful.[21,26] The polymerisation of this monomer in the presence of t-butyl peroxide, the amount of which was 50 wt.%, yielded only a trimer, and a product with a MW of 1790, a softening temperature of 165 °C, and a melting point of 270 °C was obtained only when $AlCl_3$ (~5%) was used. Dimers and trimers with a main hydrocarbon chain, carbaborane side groups, and terminal vinyl groups have also been obtained by the radiation-induced polymerisation of isopropenyl-*o*-carbaborane.[23]

A solid vitreous substance with a molecular weight of (1.0 to 7.5) $\times 10^4$ is formed from 1-allyl-*o*-carbaborane in the presence of $AlCl_3$.[21] The products of the radiolysis of 1-allyl-*o*-carbaboranes by ^{60}Co γ-rays[27] were fractionated by gel chromatography and investigated by the IR, NMR, and chromatomass-spectrometric methods. It was found that the main products comprised seven dimers with the same molecular weight of 366, differing in the positions of two double bonds in the molecule, and saturated oligomers with a degree of polymerisation of 5, independent of the radiation dose and dose rate. According to the reaction mechanism proposed, the abstraction of a hydrogen atom from the allylcarbaborane results in the formation of radicals of the allyl type whose recombination yields unsaturated dimers. The addition of a hydrogen atom to the carbaborane monomer affords radicals of the propyl type, which propagate the radical chain process with chain transfer leading to the formation of unsaturated oligomers. The chain termination in the dimer and oligomer formation processes takes place via a bimolecular mechanism.

The influence of the physical state on the radiolysis of solid alkenyl-*o*-carbaboranes, for example, 1-allyl-*o*-carbaborane,[28] has been demonstrated. 1-Allyl-*o*-carbaborane can exist in three mesomeric phases: in the temperature range from −3° to −16 °C (phase 1), from 16° to −36 °C (phase 2), and below −36 °C (phase 3). The average degree of polymerisation of the oligomers obtained by the radiolysis of the allylcarbaborane is 5 and is independent of temperature in the range from −50° to +50 °C. The results obtained have been discussed from the standpoint of the influence of the structure of the crystal lattice and diffusion-controlled processes. The authors note that the nature of the solid state, i.e. the crystallinity, plays an important role in radiolytic reactions. The dipole moments of vinyl-, isopropenyl-, and allyl-*o*-carbaboranes have been measured.[29] The quantum-chemical calculation of the charge distribution in these compounds and of the dipole moments μ with the experimental (taken from the literature) bond lengths and valence angles have been carried out by the INDO (incomplete neglect of the differential overlap of atomic orbitals) method. The calculated absolute values of μ were found to be about twice as high as the experimental values taken from the literature. However, the orientation of μ and the charge distribution, indicating the transfer of negative charge to the substituent, confirmed qualitatively, in the authors' view, the hypothesis that the free-radical oligomerisation of 1-alkenyl-*o*-carbaboranes can result in the formation of radicals, leading to the incorporation of the carbaborane fragment in the main chain. However, the carbochain polymer with carbaborane groups in the main chain is formed preferentially, which has been demonstrated convincingly by the EPR method.

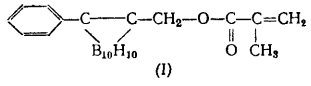
The polymerisation of monomers whose double bond is remote from the carbaborane nucleus, which promotes a decrease in the steric influence of the carbaborane group and the formation of polymers with large molecular weights, proceeds more readily. For example, 1-acryloyloxymethylene-*o*-carbaborane polymerises readily in bulk in the presence of 2% of benzoyl peroxide at 60 °C:[26]



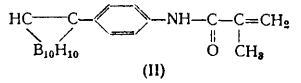
The polymer is a solid and brittle substance soluble solely in boiling terphenyl. It softens and becomes rubber-like at 165 °C. The poor solubility of this polymer is associated, according to the authors,[30] with the cross-links formed as a result of the interaction of the unsubstituted CH group of the *o*-carbaborane with the acrylic group of the growing chain. Under analogous conditions, 2-methacryloyloxymethyl-1-methyl-*o*-carbaborane affords a polymer which is readily soluble in chloroform.

A homopolymer of 1-methacryloyloxymethylene-*o*-carbaborane (MOC) with a MW of 5000 has been obtained by carrying out the reaction in benzene in the presence of 2% of azobisisobutyronitrile (ATBN).[22] Later, analysis of the structure of the MOC molecule, taking into account the remoteness of the carbaborane nucleus from the double bond, justified the assumption[31,32] that the radical polymerisation of this compound can yield products with higher molecular weights. A study of the kinetics of the radical polymerisation of MOC in benzene revealed the characteristic features of this reaction and demonstrated the influence of the concentration of the monomer in solution on the molecular weight characteristics as well as the possibility of obtaining polymers with molecular weights of (1.5–40) $\times 10^4$. The gel effect, which is so characteristic of the polymerisation of methacrylic acid esters, is absent. The orders of the polymerisation reaction with respect to the monomer and the initiator (1.28 and 0.44 respectively) and the process activation energy (17.5 kcal mol^{-1}) were determined. The polymer, with a MW of 40×10^4, begins to decompose vigorously in air at 270 °C without passing to a viscofluid state.

The synthesis and radical polymerisation in bulk of methacryloyl derivatives of *o*-carbaborane, not described previously, have been reported:[33] 1-methacryloyloxymethylene-2-phenyl-*o*-carbaborane (I) and 1-[4-(methacryloylimino)phenyl]-*o*-carbaborane (II):



(I)

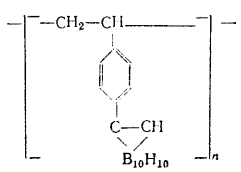


(II)

The homopolymers obtained from these monomers are colourless transparent blocks insoluble in organic solvents and characterised by a gel fraction content of up to 70%. According to the results of dynamic thermogravimetric analysis (DTGA) in air, the temperatures of the onset of decomposition of the polymers of compounds (I) and (II) are 215° and 190 °C. The formation of structured polymers may be associated, in the authors' view, with the presence in the compound synthesised of mobile hydrogen atoms both in the C—H group of the carbaborane and in the *para*-position in the benzene ring, on the one hand, and in the methylene group $-CH_2-$, which is influenced by two electron-accepting groups in the monomer (I) and by the amide hydrogen in the monomer (II), on the other.

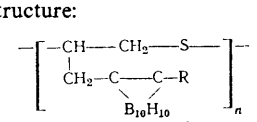
Communications explaining structure and formation in the course of the synthesis of carbaborane-containing polymers in the presence of peroxides by the involvement of free boron-centred radicals, leading to branching and to network structures have appeared recently.[34-36]

The capacity of 4-(1-*o*-carbaboranyl)styrene for polymerisation under various conditions has been investigatged.[37] Polymers with the highest molecular weight (up to 6×10^4) and a softening temperature of 280—240 °C have been obtained by thermal polymerisation at 160—200 °C. In the presence of radical initiators, polymers with a MW of $\sim 1.2 \times 10^4$ and a softening temperature of 320 to 340 °C are formed. Polymerisation via the anionic mechanism takes place slowly, while that involving the cationic mechanism does not occur at all. On the basis of the IR spectra of the polymers, the authors suggested that the polymerisation takes place in all cases via the vinyl group and that the polymer has the following structure:



The polymerisation of *p*-(*o*-carbaboranyl)phenylacetylene in solution in aromatic solvents in the presence of triphenylphosphine-nickel acetylacetonate has been investigated.[38] The use of this catalyst made it possible to obtain linear polyconjugated carbaborane-containing oligophenylacetylenes with MW of 1230—1320. A mechanism has been proposed for the formation of the active centre and the chain propagation. The oligomers synthesised are thermoplastics with a softening temperature of 80—115 °C.

The ionic polymerisation, with ring opening, of 3-[alkyl(aryl)-*o*-carbaboranyl]-1,2-epithiopropanes in bulk and in solution has been investigated[39] in order to obtain polymerisation polysulphides with enhanced solubility and thermal stability. Polymers with the highest molecular weight (2.5×10^5) were obtained via the anionic mechanism in solution using specially synthesised cyclic cadmium carbaboranylthiolates as initiators. Cationic polymerisation under the influence of BF_3 etherate takes place even at -20 °C, but it leads to polymers with a lower molecular weight (1.7×10^4). Polycarbaboranyl sulphides with the *o*-carbaborane group in the side chain are amorphous substances softening at 50—120 °C, which apparently have the following structure:



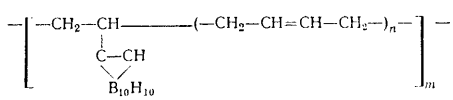
R=C_6H_5, $(CH_3)_2CH$;
n=60—970

According to DTGA data, the temperatures corresponding to a 5% weight loss by these polymers are 250—300 °C.

There are only a few literature data on the three-dimensional polymerisation of bifunctional unsaturated carbaborane-containing monomers. Carbochain cross-linked carbaborane polymers have been obtained by the radical polymerisation of unsaturated compounds with two allyl or acryloyl groups.[40,41] Thus the network polymer based on diallyl *m*-carbaboranedicarboxylate[40] with a glass point of 300 °C has been synthesised in bulk in the presence of a mixture of benzoyl peroxide and t-butyl peroxide as initiators. There is a good correspondence between the experimental and calculated glass points, which indicates the virtually complete conversion of the double bonds of the allyl groups. The polymerisation of di(acryloyloxymethylene)-*o*-carbaborane in the presence of peroxide initiators has been investigated by IR spectroscopy and differential thermal analysis.[41] It was shown tht the most effective initiator of the polymerisation leading to the formation of thermostable polymers is dicumenyl peroxide.

Thus, despite the difficulties encountered by investigators in the study of the homopolymerisation of carbaborane-containing compounds, definite advances have been achieved in this field in recent years and polymers with high molecular weight (MW up to 10^5) have been synthesised.

Unsaturated carbaborane-containing compounds are known to copolymerise readily with various vinyl polymers. Thus a rubber-like product having the following structure has been obtained by the copolymerisation of vinyl-*o*-carbaborane with butadiene:[21]



n = 5 or 7.

The copolymers of isopropenyl-*o*-carbaborane with butadiene have been synthesised by radical copolymerisation in bulk (the molecular weight did not exceed 1000)[42] and in emulsion.[43] The copolymer of acryloyloxymethylene-*o*-carbaborane with butadiene has been obtained in emulsion.[44] The radical copolymerisation of vinyl-*o*-carbaborane with allyl-*o*-carbaborane and 1-isopropenyl-*o*-carbaborane-2-carboxylic acid results in the formation of copolymers with MW of $(6-55) \times 10^3$.[21]

The synthesis of carbaborane-containing oligomers based on isoprene and vinyl- and isopropenyl-*o*-carbaboranes, with the copolymerisation initiated by hydrogen peroxide and cumenyl hydroperoxide in solution in alcohol, has been described.[45] The copolymerisation constants for the systems investigated were calculated by the integral Mayo—Lewis method and the low activity of alkenylcarbaboranes in copolymerisation with dienes was demonstrated. The oligomers obtained had molecular weights ranging from 2000 to 3340 and contained terminal hydroxy-groups. On the basis of the dependence of the degree of polymerisation on the concentration of monomers and the bifunctional nature of the oligomer, the authors suggested that chain termination takes place via a recombination reaction and that the reactions involving chain transfer from the alkenylcarbaborane group to the monomers and the solvent do not take place.

The copolymerisation of ispropenyl-*o*-carbaborane with methyl acrylate (MA) in the presence of AIBN produces a copolymer whose boron content depends on the concentration of isopropenyl-*o*-carbaborane in the initial mixture.[26,46] The copolymer, containing 22% of

boron, is a vitreous substance with a softening temperature of 45 to 80 °C, while the copolymer with 10% of boron softens at 45 – 50 °C. Copolymers with approximately the same boron content are formed in the copolymerisation of MA with vinyl-*o*-carbaborane.[46]

In contrast to MA, methyl methacrylate (MMA) hardly copolymerises with isopropenyl-*o*-carbaborane in solution in toluene in the presence of ATBN.[47] Vinyl-*o*-carbaborane does not copolymerise with MMA under these conditions either. The higher reactivity of vinyl- and isopropenyl-*o*-carbaboranes in copolymerisation with MA compared with MMA is due to the smaller steric hindrance and the higher activity of the macroradicals with terminal MA units.[46]

Both these carbaborane-containing monomers are relatively inactive in copolymeristion with styrene, which is indicated by the low boron content (not more than 4%) in the copolymers formed. Later it was possible to obtain[48] copolymers of the above monomers with *p*-chlorostyrene and *p*-methoxystyrene, in which the boron content reached 25 – 50% of the theoretical value.

Analogous results have been obtained in the copolymerisation 2-ferrocenyl-1-vinyl-*o*-carbaborane and 2-ferrocenyl-1-isopropenyl-*o*-carbaborane with styrene in MMA.[49] It was shown that both ferrocenyl-*o*-carbaboranes enter into the composition of the copolymers with MMA in an extremely limited amount and are much more active in copolymerisation with styrene. Furthermore, in all cases an increase in the content of the ferrocenyl-*o*-carbaboranes in the initial mixture reduces the molecular weight of the copolymers.

A copolymer of methacryloyloxymethylene-*o*-carbaborane with acryloylferrocene, having a MW of 3×10^4, and a copolymer of vinylferrocene, isopropenyl-*o*-carbaborane, and isoprene have also been synthesised.[50]

The radical copolymerisation of acryloyloxymethylene-*o*-carbaborane with fluorinated acrylates has been carried out in bulk and in emulsion.[26,51] Some of these copolymers are rubber-like substances with an MW of 2.3×10^3, soluble in acetone, ethyl methyl ketone, or diethyl ketone.

Copolymers with a boron content up to 24% have been obtained by the radical copolymerisation of 1-methacryloyloxymethylene-2-phenyl-*o*-carbaborane (I) and MMA in bulk in the presence of benzoyl peroxide.[52] It was found that the copolymers are enriched in MMA units for any initial monomer ratios. With increase in the fraction of the carbaborane compound (I), the softening temperature and the temperature of the onset of decomposition of the copolymers increase together with the yield of the coke residue. The copolymerisation under the same conditions of MMA with 1-[4-(methacryloylimino)phenyl]-*o*-carbaborane (II), the content of the latter in the reaction mixture not exceeding 5 mole % (limiting solubility),[52] results in the formation of copolymers with $\overline{M}_w$ = (9.1 to 10.8) $\times 10^4$ and polydispersity coefficients $\overline{M}_w/\overline{M}_n$ of 1.53 – 2.31.

In order to modify low-density polyethylene, the radical copolymerisation of ethylene with isopropenyl-*o*-carbaborane was carried out at a pressure of 1400 kg cm^{-1} and 160 °C in bulk and in solution.[53] It was shown that the rate of reaction and the molecular weight of the copolymers decrease with increase in the content of the carbaborane monomer in the reaction mixture. For a low overall degree of conversion of the monomers and a low content of isopropenyl-*o*-carbaborane in the initial mixture (up to 15 mole %), this relative activity proved to be higher than that of ethylene. The copolymers are plastic solids soluble in aromatic hydrocarbons and giving rise to elastic films on pressing at 130 – 170 °C. The influence of γ-radiation on copolymers containing 0.55 – 2.70 mole % of isopropenyl-*o*-carbaborane has been studied.[54] Measurements of the strength properties of the copolymers have shown that, for a low content of boron, their radiation stability is close to that of polyethylene. It has also been established that the resistance of the copolymers to thermo-oxidation diminishes after γ-irradiation.

The copolymerisation of vinyl-*o*-carbaborane with styrene in proportions of 1 : 3, initiated by γ-rays, has been investigated.[55] It was shown that the copolymer consists of 11 – 12 units and that there are approximately nine styrene units for two vinyl-*o*-carbaborane units. The structure of the copolymer was studied by NMR and flash pyrolysis; it softens up to 85 °C and melts at 105 °C.

Copolymers containing terminal hydroxy- or carboxy-groups have been synthesised by the copolymerisation of vinyl-*o*-carbaborane, isopropenyl-*o*-carbaborane, and acryloyloxymethylene-*o*-carbaborane with isoprene, butadiene, and chloroprene in solution at 65 °C in the presence of 4,4′-azobis(4-cyano-1-pentanol) or 4,4′-azobis(4-cyanovaleric) acid.[56] It has been noted that the large difference between the polarities of the comonomers ensures the ease of copolymerisation. The M_n of the copolymers are 2200 – 7400 and M_w/M_n = 1.38 to 1.85. In all cases, the yield and the molecular weight of the copolymers decrease with increase in the content of the unsaturated derivatives of *o*-carbaborane in the reaction mixture from 5 to 50 wt.%.

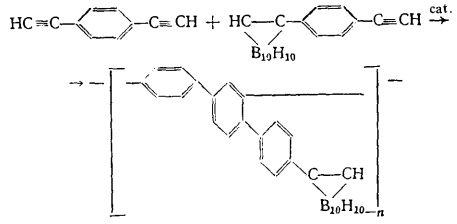
A copolymer of MMA and 4-(1-*o*-carbaboranyl)styrene with a MW of 3.08×10^4 and a softening temperature of 172 – 220 °C has been obtained.[37] While according to DTGA data a weight loss of 2% by PMMA is observed at 100 °C, the above copolymer loses 2% of its weight at 250 °C. Subsequently the authors[57,58] carried out the radical and thermal copolymerisation of 4-(1-*o*-carbaboranyl)styrene with MMA, isoprene, and acryloylferrocene. The copolymers synthesised with MW up to 2.8×10^4 were tested by the thermomechanical method and the stress relaxation method under scanning conditions. It was shown that, owing to the heterounit nature of the copolymers, their thermal characteristics (the glass point and the temperature of the onset of weight loss) vary both additively (copolymers with MMA) and non-additively (copolymers with isoprene). For the copolymers with acryloylferrocene,[58] a smooth increase in the glass point and the non-additive variation of the thermal stability are observed with increase in their content of carbaborane units.

In order to increase the thermo-oxidative stability of PMMA, network copolymers of MMA with bifunctional unsaturated isomeric derivatives of carbaboranes—the diallyl esters of *m*- and *p*-carbaboranedicarboxylic acids[59,60] and 1,2-di(methacryloyloxymethylene)-*o*-carbaborane [61,62]—were synthesised in bulk via a radical mechanism. Investigation of the thermo-oxidative degradation of all the copolymers obtained showed that the introduction from 0.1 to 0.5 mole % of *m*- and *o*-carbaborane fragments into the PMMA chain increases sharply the thermo-oxidative stability of the polymer, while the presence of *p*-carbaborane nuclei in the copolymer structure reduces such stability. It has been suggested that small amounts of *m*- and *o*-carbaborane act as inhibitors of radical-chain processes.

The thermal and mechanical relaxation properties of network copolymers of MMA and the diallyl ester of *m*-carbaboranedicarboxylic acid of different composition have been investigated and the network structure has been determined from the comparison of the experimental and calculated glass points.[40] It has been found that, at a high concentration of the carbaborane comonomer, the network consists of two components, one of which is the product of the interaction of MMA with part of the diallyl *m*-carbaboranedicarboxylate used in the reaction, while the second is a network based on the homopolymer of the carbaborane monomer. This results in the formation of specimens having two main transition

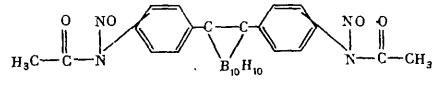
temperatures and two regions of relaxation processes of different intensity.

The joint polycyclotrimerisation of *p*-(*o*-carbaboranyl)phenylacetylene with *p*-diethynylbenzene in the presence of $NiCl_2.2PPh_3.2NaBH_4$ or $Al(iso\text{-}C_4H_9).TiCl_4$ in accordance with the scheme:[63]

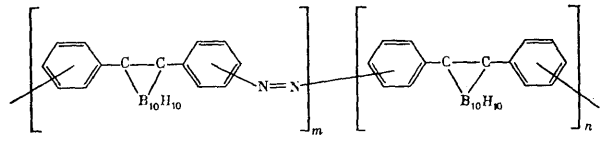


has been achieved. The interaction of equimolar amounts of the starting materials yielded co-oligophenylenecarbaboranes soluble in toluene and having a high boron content. With increase in the amount of *p*-(*o*-carbaboranyl)phenylacetylene in the initial mixture, the yield of the oligomer and its molecular weight decrease (from 78 to 20% and from 3350 to 1020 respectively). *o*-Carbaborane-containing oligophenylenes are characterised by high thermal and thermo-oxidative stabilities. Furthermore, they are regarded[64] as ligands for the synthesis of π-arene complexes of chromium carbonyl. The use of the "triphenylphosphine–nickel acetylacetonate" catalytic system in the copolymerisation of *p*-(*o*-carbaboranyl)phenylacetylene and *p*-diethynylbenzene made it possible to obtain thermoreactive carbaborane-containing polyarylacetylenes in yields up to 93% and with a higher molecular weight.

The recombination of the phenyl and azophenylene products of the decomposition of 1,2-di(*N*-nitrosoacetamidophenyl)-*o*-carbaborane (DC), i.e.



yielded *o*-carbaborane-containing polyazophenylene (PAPC) having the following structure:[65,66]



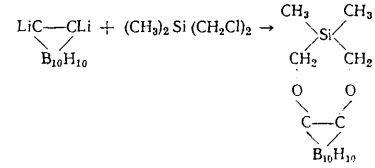
By combining the processes involving the recombination of the DC decomposition products with processes involving the radical polymerisation of various vinyl monomers, it is possible to obtain copolymers with carbaborane units. Thus copolymers containing between 4 and 38% of PAPC fragments have been synthesised by the emulsion copolymerisation of styrene with DC decomposition products. It was shown that the introduction of the carbaborane fragments into the macromolecules of polystyrene increases significantly the thermo-oxidative stability of the latter.

The influence of the nature of unsaturated *m*- and *p*-carbaborane-containing polyethers on their capacity for copolymerisation with vinyl compounds in bulk, solution, and emulsion in the presence of radical and ionic initiators under the influence of γ-radiation or high pressure has been examined.[67,68] The vinyl comonomers used were styrene, acrylonitrile, and 1,1,2-trichlorobuta-1,3-diene. It was found that the copolymers of carbaborane-containing unsaturated polyethers are characterised by a higher resistance to thermo-oxidation and by more effective adhesion parameters compared with the analogous copolymers in which there are no carbaborane groups.

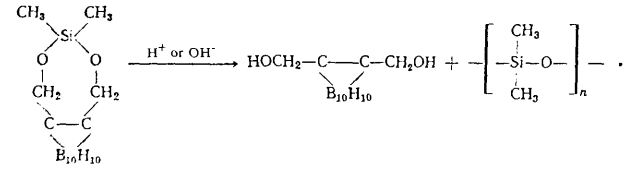
Polymers and copolymers based on alkenylcarbaboranes can be used in various fields: as plasticisers and combustion catalysts,[44] as materials with enhanced thermo-oxidative stability,[59] in adhesives in order to increase their thermal stability,[69,70] for the preparation of anion-exchange resins,[71] and for the modification of rubbers.[72,73]

III. SILICON-CARBORANE-CONTAINING POLYMERS

It is known[15] that the polymers in which hydrolytic and chemical stability is combined with high thermal stability include silicon-carbaborane-containing polymers. The first attempts to synthesise such compounds by polymerisation and polycondensation methods were unsuccessful, since the initial *o*-carbaborane-siloxane derivatives exhibited a high tendency towards the formation of stable cyclic systems. This occurred apparently as a consequence of the adjacent location of the carbon atoms in the *o*-carbaborane nucleus involved in an ordinary covalent C–C bond whose length (1.64–1.67 Å) greatly exceeded the length of the ordinary covalent C–C bond in olefins (1.54 Å), which in fact favoured the formation of exocyclic derivatives.[74–76] For example, a stable cyclic product has been obtained by the interaction of dilithio-*o*-carbaborane with di(chloromethyl)dimethylsilane:[77]

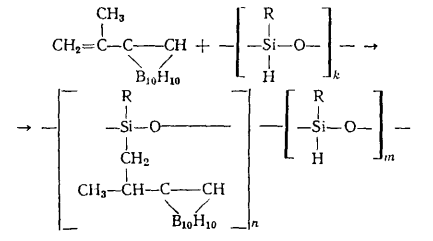


The reaction of 1,2-di(hydroxymethylene)-*o*-carbaborane with dichlorodimethylsilane also results in the formation of a seven-membered cyclic compound.[78] When an attempt is made to open this ring in order to obtain a linear polymer, hydrolysis leads to the reformation of the initial carbaboranediol and polydimethylsiloxane:



For this reason studies were continued on the synthesis of monosilyl-*o*-carbaborane monomers from which various polymers containing *o*-carbaborane groups in the side chain were synthesised by polycondensation reactions.

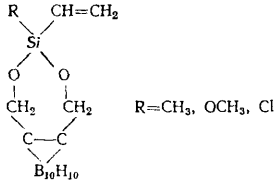
There are few available literature data on the synthesis of carbaborane-siloxane polymers. Polysiloxanes containing *o*-carbaborane nuclei in the side chain have been obtained by the migration copolymerisation of isopropenyl-*o*-carbaborane with the polyalkylhydrosiloxanes:[79,80]



R=CH_3, C_2H_5, C_6H_5; $k=n+m$.

Studies have shown that, in the absence of the catalyst below 200 °C, the reaction hardly occurs and that even at high temperatures the rates of copolymerisation remain low, which can be accounted for by the electron deficiency of the carbaborane nucleus, deactivating the neighbouring unsaturated bond, and by steric hindrance. With increase in the boron content in the polymer, the solubility of the latter in aromatic hydrocarbons and alcohols diminishes. According to DTGA data, the above polymers are stable in air up to 400 to 500 °C.

Carbochain silicon-carbaborane-containing polymers have been synthesised by the radical polymerisation in bulk of carbaborane-containing exocyclic vinylsilanes with various substituents at the silicon atom:[81,82]



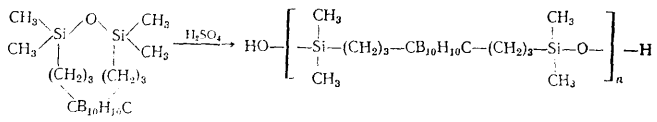
A mixture of benzoyl peroxide and t-butyl peroxide was used as the initiator. It was established that, in the polymerisation of the compounds with R = CH_3, only the dimer is formed, while in other cases insoluble homopolymers were obtained in yields up to 80%. The copolymerisation of the above vinylsilanes with MMA and styrene was achieved under the same conditions for different monomer ratios.[81-83] The copolymerisation with MMA yielded both linear soluble copolymers with a MW of $(4.0-6.9) \times 10^5$ and three-dimensional copolymers; linear copolymers with styrene have molecular weights up to 1.6×10^5. The formation of insoluble polymers and copolymers with MMA is determined by the fact that in certain cases homo- and co-polymerisation not only occurs via the vinyl group but is also accompanied by the partial ring opening and condensation of the resulting silanol groups SiOH.[82] The influence of the substituent at the silicon atom on the reactivity of the exocyclic compounds has been examined and it has been shown that the monomer with R = OCH_3 shows the greatest activity in the copolymerisation reaction. It has been noted that, with increase in the content of the silicon-carbaborane compound in the reaction mixture, its mole fraction in the copolymer also increases and the yield and the molecular weight of the copolymer diminish. Furthermore, the temperatures of the onset of weight loss by the copolymers and yield of the coke residue increase with increase in the mole fraction of the exocyclic derivative in the copolymer, while the softening temperatures decrease.

The migration copolymerisation reaction of epoxypropoxypropyltriethoxysilane with 1,2-di(hydroxymethylene)-*o*-carbaborane, which takes place with formation of a linear oligomer in the first stage, has been investigated.[80,84] In the second stage, the content of the epoxy-groups reaches a minimum, the ethoxy-groups undergo alcoholysis, and the product passes from the viscofluid state to the elastic state.

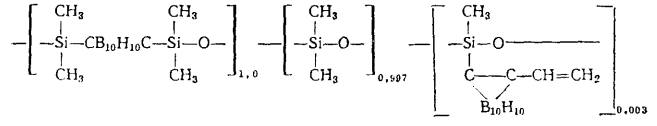
The study of the deformation thermal stability of siloxanecarbaborane oligoethers showed[84] that, in contrast to the majority of polymers, the product does not soften and does not melt with increase in temperature its volume increasing under these conditions at temperature above 360 °C. In view of the high thermal stability of the oligomers obtained, in which effective adhesion to glass and metal is combined with good dielectric properties, they can be used as thermoinsulating coatings.

The failure of the attempt to synthesise silyl-*o*-carbaborane compounds with a linear structure stimulated investigators to turn to *m*-carbaborane systems, in which the adjacent positions of the carbon atoms rule out the possibility of the formation of exocyclic structures. The stability at high temperatures is retained in these systems.

Thus an elastomeric *m*-carbaborane-containing polysiloxane with a molecular weight of 8500 has been obtained by the polymerisation of cyclic *m*-carboranylenesiloxane in the presence of acid catalysts:[85]



From the practical point of view, the synthesis of poly-*m*-carbaborane-siloxanes has been an important advance in the development of thermostable carbaborane elastomers.[6,86,87] These polymers (given the brand name "Decsil") consist of dialkyl- or diaryl-siloxane units linked by *m*-carbaborane groups and are obtained by the polycondensation of *m*-carbaborane-containing chlorosilanes and alkoxysilanes in the presence of $FeCl_3$ as catalyst. The high thermo-oxidative stability and the effective mechanical and elastic properties of the above polymers have served as a precondition for the development of a technology of the preparation of thermostable siloxane-carbaborane rubbers.[88-90] Polymers with the brand name "Decsil-201", in which some of the methyl groups have been substituted by vinyl derivatives of *o*-carbaborane, have been synthesised for this purpose:



This made it possible to carry out hardening via a free-radical mechanism.

There have been communications[91-93] about the synthesis by analogy with Decsils, of carbaborane-siloxane elastomers containing the carbaboranes $C_2B_5H_7$ and $C_2B_8H_{10}$ in the siloxane chain. In order to prevent their crystallisation and to improve their elasticity, these elastomers were modified by introducing 5–20% of vinyl-*o*-carbaborane into the main or side chain.[94,95] It was established that heating of such modified polymers in nitrogen to 350 °C and in air to 250 °C has no appreciable influence on the glass point and that even the solubility of the polymer in xylene is retained under these conditions. After heating in an atmosphere of nitrogen to 550 °C, the polymers are cross-linked.

Summarising the analysis of the literature data on the polymerisation and copolymerisation of silicon-carbaborane-containing monomers, one may conclude that the polymerisation methods of synthesis of silicon-carbaborane-containing polymers have been little investigated hitherto. This is also indicated by the reviews published in recent years,[17,18,96-98] which have been mainly devoted to questions of the preparation of carbaborane-siloxane polymers by polycondensation methods.

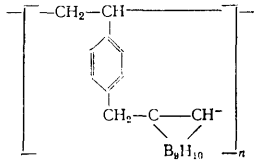
IV. POLYMERS CONTAINING DICARBAUNDECABORATE FRAGMENTS

Apart from polyhedral carbaboranes, i.e. carbaboranes with a closed structure (*closo*-carbaboranes), open carbaborane structures of

nido-carbaboranes are known. On interaction with nucleophiles such as alkali metal alkoxides[19] or amines,[99] *o*- and *m*-carbaboranes(12), are cleaved selectively with abstraction of the boron atom from the third position in the *o*- and *m*-carbaborane nuclei with formation of dicarbaundecaborates(13) anions. Such anions are acids and on treatment with NaH they split off a proton and afford the dicarbollide ion (Fig.1).[100]

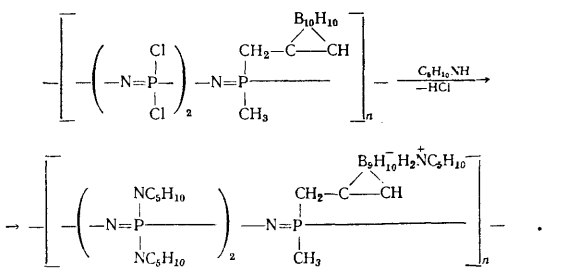
The negative charge on the dicarbaundecaborate anion leads to the appearance in the system of an electron-donating effect via inductive and resonance mechanisms, in contrast to the neutral *C*-carbaboranyl groups, which exhibit electron-accepting properties. Thus the electron-donating effect of the (3)-1,2-dicarbaundecaborate group is manifested in the pK_a values for the carboxylic acids of the (3)-1,2-dicarbaundecaborate group is manifested in the pK_a values for the carboxylic acids of the (3)-1,2-dicarbaundecaborate series (6.9–7.3 in 50% ethanol), which are very weak acids compared with carbaboranecarboxylic acids.[101]

Methods are known for the preparation of polymers with dicarbaundecaborate fragments[102–104] whose carbaborane nuclei are cleaved by alkalies or amines. However, these are multistage procedures and each stage takes 3–8 days. Thus, in studies by Hawthorne and co-workers,[102,103] polystyrene cross-linked with 1% of divinylbenzene was made to undergo successive reactions in accordance with the following scheme: (1) chloromethylation of polystyrene; (2) cleavage of *o*-carbaborane with alcoholic alkali to the dicarbaundecaborate anion; (3) preparation of the dicarbollide ion $(7,8\text{-}C_2B_9H_{11})^{2-}$; (4) reaction of the chloromethylated polystyrene with the dicarbollide ion leading to the formation of a polymer with dicarbaundecaborate groups:



Rudolph and co-workers[104] also obtained the above polymers from cross-linked polystyrene in accordance with the following scheme: (1) chloromethylation of polystyrene; (2) preparation of *o*-carbaboranyl-lithium with chloromethylated polystyrene; (4) cleavage with piperidine of the carbaborane linked to polystyrene to give the dicarbaundecaborate anion.

Later Allcock et al.[105] obtained *nido*-carbaboranylpolyphosphazenes by the interaction of carbaborane-containing polyphosphazenes with piperidine in solution in tetrahydrofuran:



Different reactions of *m*-carborane-containing polymers are very frequently accompanied by the cleavage of their *m*-carbaborane nucleus to the dicarbaundecaborate anion. This happens, for example, on heating *m*-carbaborane-containing polyamides in dimethylformamide and concentrated alkalies,[106] in their thermal and thermo-oxidative degradation,[107] in the cyclodehydration of *m*-carbaborane-containing polyaminoamides and polyhydroxamides,[108,109] and also in the formation of polyamides based on *m*-carbaboranyl-enediamine and the dichlorides of aromatic acids.[110] All these reactions result in the formation of heterounit polymers, whose properties depend on their content of dicarbaundecaborate groups.

Later Korshak, Bekasova, and co-workers[111–113] obtained heterounit *m*-carborane-containing polyamides by treatment with nucleophiles and demonstrated by ^1H NMR that the maximum attainable content of dicarbaundecaborate fragments, without degradation, in such polymers is about 50%. Polyamides differ from the starting materials in their solubility and chemical and therm-oxidative stability.

As already mentioned in the introduction, up to 1984 there was no information whatever in the literature about the preparation of polymers with dicarbaundecaborate fragments by the polymerisation or copolymerisation method. It is known that vinyl derivatives of *o*-carbaborane show a low reactivity in the radical polymerisation reaction. It was shown for the first time in a number of studies[114–117] in relation to 1-isopropenyl-*o*-carbaborane that the transition from neutral *closo*-carbaboranes to negatively charged *nido*-carbaborane structures facilitates the copolymerisation reaction of their unsaturated derivatives and it was established that the latter are capable of copolymerisation with vinyl monomers. The salts of 1-isopropenyl-(3)-1,2-dicarbaundecaborate (IDC) synthesised do not polymerise via radical and ionic mechanisms, but, in contrast to 1-isopropenyl-*o*-carbaborane,[47] enter into the copolymerisation reaction with MMA

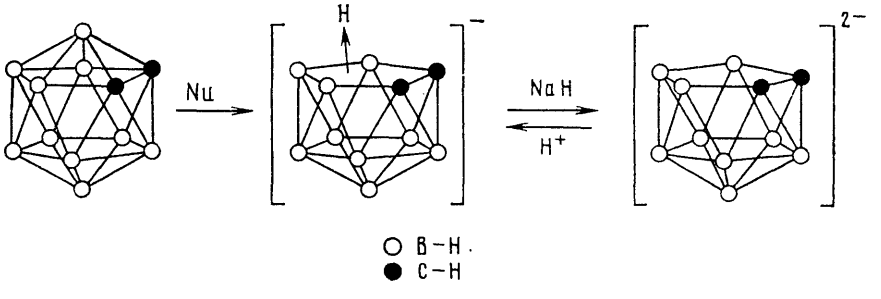
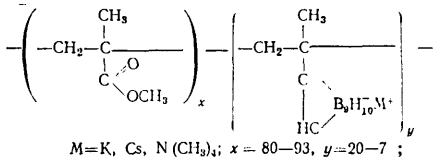
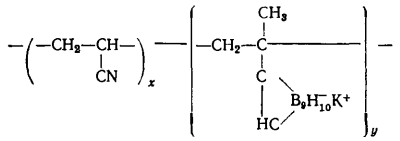


Figure 1. Scheme for the preparation of the dicarbaundecaborate(13) anion and the dicarbollide ion.[100]

and acrylonitrile, forming copolymers containing dicarbaundecaborate fragments:



M=K, Cs, $N(CH_3)_4$; $x = 80-93$, $y = 20-7$;



$x=50-99$, $y=50-1$.

The radical copolymerisation was carried out in solution at 60 to 80 °C in the presence of AIBN. The dependence of the yield, the intrinsic viscosity, and the composition of the copolymers on the reaction conditions was investigated[115,117] and the optimum parameters of the synthesis were determined. It was shown that the reactivity of the IDC salts in the copolymerisation with acrylonitrile is higher than in the copolymerisation with MMA: in the former case, it is possible to introduce up to 50 mole % of the dicarbaundecaborate units into the copolymer, while in the latter up to 20 mole % can be introduced. The molecular weights of the copolymers with acrylonitrile and MMA reach 5.0×10^4 and $(2.5-5.2) \times 10^4$ respectively. It was found that the yield and molecular weight of the copolymer diminish with increase in the mole fraction of the dicarbaundecaborate and also with increase in the ionic radius of the salt cation, which is caused in all probability by steric factors.

Copolymers of this kind are of interest also because they contain dicarbaundecaborate groups capable of behaving as ligands in transition metal complexes. For this reason, the copolymers of MMA with IDC salts have been used as polymer matrices in the synthesis of polymeric metallocarbaborane complexes (Fig.2).[114,116] A characteristic feature of the structure of these complexes is the fact that the dicarbollyl ligand of the metallocarbaborane is linked directly via a carbon atom to the main chain of the polymer matrix. The structure has been confirmed by elemental analysis, IR spectroscopy, and ^{31}P NMR. The catalytic activity of the synthesised phosphinocarbaborane complexes of rhodium in hydrogenation and isomerisation reactions of unsatuated hydrocarbons was investigated[114,118] and it was shown that these complexes are much more effective catalysts of the above reactions than the carbaboranerhodium complexes fixed on polystyrene which had been known previously.[102-104]

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Thus, the literature data presented show that the use of homo- and co-polymerisation methods for the synthesis of carbaborane-containing polymers makes it possible both to obtain new high-molecular-weight compounds and to modify the known polymers and to impart to the latter properties of practical importance. The study of the polymerisation of unsaturted derivatives of dicarbaundecaborates and of the properties of the polymers formed is of great interest.

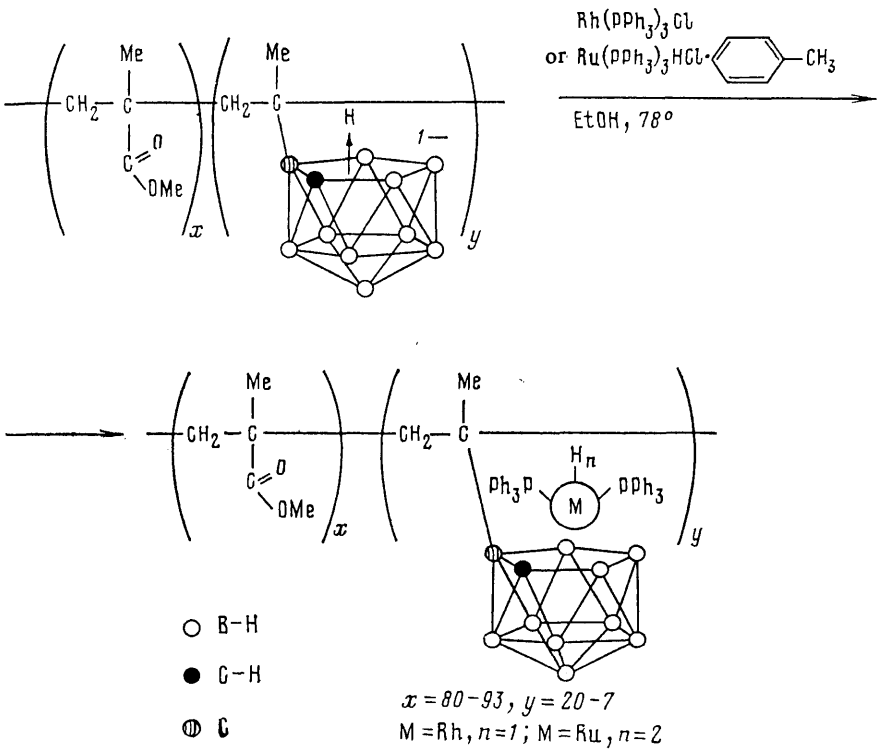


Figure 2. Scheme for the preparation of polymeric phosphinocarbaborane complexes of rhodium(I) and ruthenium(II).[114,116]

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Phosphite Synthesis of Oligodeoxyribonucleotides

N.N.Karpyshev

Data in the literature published between 1983 and 1986 on the synthesis of oligodeoxyribonucleotides from nucleoside derivatives of phosphorous acid are reviewed. Attention is mainly focused on the techniques employed for preparing initial monomers for condensation. The individual stages in the solid-phase phosphite method are presented, and the potential of various approaches for achieving this type of synthesis is discussed. In addition, studies on the synthesis of oligonucleotides with the aid of monoesters of phosphorous acid (phosphonate synthesis) are assessed.
The bibliography includes 101 references.

CONTENTS

I. Introduction 886
II. Synthesis of nucleoside phosphoramidites 886
III. Reactions and reagents for solid-phase phosphite triester synthesis 890
IV. Nucleoside phosphites for synthesis of oligonucleotides (phosphonate synthesis) 892
V. Phosphite reagents for introduction of different functional groups into oligonucleotides 893

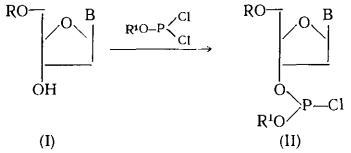
I. INTRODUCTION

Chemical synthesis of DNA fragments is of key importance for the advancement of molecular biology and genetic engineering. Many commercial organisations in a number of Advanced Nations offer a range of reagents and efficient automatic synthesisers and also provide a service for synthesising oligodeoxyribonucleotides with the required sequence. Moreover many scientific centres are involved in the elaboration of synthetic methods and therefore one would anticipate further progress in this field.

Until recently advances in solid-phase synthesis of DNA had been mainly determined by developments in the chemistry of derivatives of tri-coordinated phosphorus, the nucleoside phosphites. The reviews present in the literature at the time when the present communication was submitted for publication did not consider aspects of phosphite synthesis in any detail.[1-5] The present review focuses on reports published between 1983 and 1986 in which nucleoside phosphites were used for oligonucleotide synthesis and which deal with various practical aspects of this type of synthesis.

II. SYNTHESIS OF NUCLEOSIDE PHOSPHORAMIDITES

It is generally accepted that the original monomeric units in solid-phase phosphite synthesis were the nucleoside chlorophosphites (II) obtained by the reaction between nucleosides‡ (I) and alkyl dichlorophosphites:[6-8]



(I) (II)

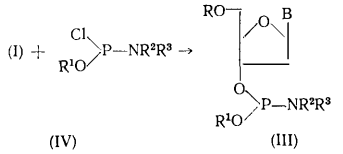
†The prefix *d* (deoxy) is omitted throughout for brevity.

‡The following arbitrary terms are used to describe the formulae: $(CH_3O)_2Tr$ – 4,4'-4,4'-dimethoxytrityl; throughout where not specially indicated R, triarylmethyl: R^1, alkyl or aryl; R^2 and R^3, alkyl; B, the protected heterocyclic base of the nucleoside.

Although this appears to be a straightforward process, the monomers (II) are relatively unstable during storage, and it is necessary to employ low temperatures (–78 °C), in order to reduce secondary reactions. Although until recently certain groups of research workers have adhered to the chlorophosphite approach[9] for this synthesis, the use of phosphoramidites (III) has gained universal acceptance, since the latter compounds may be converted into active intermediates by reaction with acidic reagents *in situ*.[10] A feature of this approach is the relative ease of use of these compounds, and they can be stored for months or even years under conditions which are easy to provide in practice. There are currently several techniques and modifications for preparing various phosphoramidites (III). Naturally not all of these modifications are used in practice but they all represent "progress steps" along the route towards a more efficient and cost effective method for the chemical synthesis of DNA.

1. Main Methods for Monomer Synthesis

The most extensively used method for preparing phosphoramidites (III) involves the reaction between the corresponding nucleoside (I) and the following type of phosphorylating agent (IV):[10-17]



(IV) (III)

This method is quite straightforward and well-defined provided that the phosphorylating agent (IV) is pure. In addition to synthesis of normal phosphoramidites (III) this method is also used for resolving certain non-routine problems, for example preparation of phosphoramidites of unusual nucleosides,[18] and also in a number of lipids.[19]

A considerable number of type (IV) agents have already been synthesised and characterised. Key information on certain of these compounds is presented in Table 1. Nevertheless, the preparation of compounds (IV) is labour-intensive and is not always a safe process (on account of their very high reactivity). Moreover, reagent (IV)

cannot be purified by distillation, when relatively high molecular weight substituents are present in positions R^1, R^2, or R^3. Hence, several alternative routes for the synthesis of nucleoside phosphoramidites (III) have been proposed which circumvent the phosphorylating agent (IV) preparation stage. In one of these methods,[20-24] a substituted dichlorophosphite is treated with excess of triazole or its trimethylsilyl derivative. The resultant bis-triazolide subsequently reacts sequentially with nucleoside (I) and the corresponding amine:

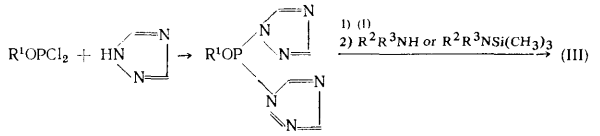


Table 1. Physicochemical properties of certain amidochlorophosphites (IV).

R^1—	—NR^2R^3	Boiling point, °C (mm Hg)	^{31}P NMR, p.p.m.	Refs.
CH_3—	—$N(CH_3)_2$	40—42 (13)	—179.5 (a)	[10]
CH_3—	—N O	52—54 (0.1)	—172.1 (a)	[11,17]
CH_3—	—$N[CH(CH_3)_2]_2$	35—36 (0.02)	—183.9 (a)	[11]
CH_3—	—N	28—30 (0.01)	—182.7 (a)	[11]
CH_3—	—N	61—64 (0.02)	—194.4 (a)	[11]
$N{\equiv}CCH_2CH_2$—	—$N(CH_3)_2$	90—92 (0.6)	—176.0 (6)	[12,16]
$N{\equiv}CCH_2CH_2$—	—$N[CH(CH_3)_2]_2$	103—104 (0.08)	—179.8 (6)	[12,16]
$N{\equiv}CCH_2CH_2$—	—N O	—	—168.2 (6)	[12,16]
$CH_3S(=O)_2CH_2CH_2$—	—N O	—	—167.5 (6)	[13]

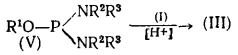
*Relative to H_3PO_4, solvent is indicated in the brackets: a) deuterochloroform; b) deuteroacetonitrile.

Conversion of the dichlorophosphite into the bis-triazolide leads to enhanced selectivity with respect to phosphorylation of nucleoside (I), i.e. a reduction in the proportion of by-products, 3',3'-dinucleoside phosphite. A similar result may also be obtained, when nucleoside (I) is treated with a large excess of dichlorophosphite R^1OPCl_2 with subsequent introduction of an adequate amount of amine:[25]

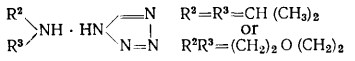
$$R^1OPCl_2 \xrightarrow{(I)} [(II)] \xrightarrow{R^2R^3NH} (III)$$

The latter method is of course only practicable, when a sufficiently effective technique (e.g. chromatography) is available for isolating the required phosphoramidite (III) from the multi-component reaction mixture.

The research workers who introduced the phosphoramidite method accept that this technique, used for activation of amides (III) with weak acids thereby creating an internucleotide linkage, is based on fundamental studies (mainly Soviet) on the protonation of amides of phosphorous acids (see communication[10] and the references in this article). Although specific questions in regard to the mechanism of protonation are still under debate,[26] this in no way imposes restrictions on the practical exploitation of the reaction in nucleic acid chemistry. For example, since bis(dialkylamino)alkoxyphosphines (V) are protonated by weaker acids than the phosphoramidites (III), the latter may be obtained by the reaction between nucleosides (I) and reagents (V) in the presence of specially selected proton donors:

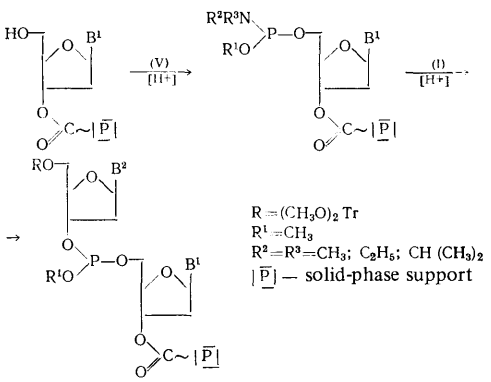


A number of azoles, of which 4,5-dichloro-imidazole proved to be the most effective,[27,28] were selected as weak acids for activation of bis(pyrrolidino)methoxyphosphine (V), $R^1 = CH_3$, $R^2R^3 = (CH_2)_4$. Another group of workers[29] have proposed that tetrazolium salts of the corresponding dialkylamines should be used for the selective activation of phosphines (V), $R^1 = CH_3$.



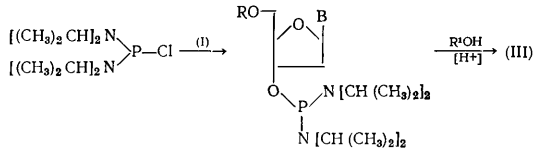
The possiblity of obtaining phosphoramidites (III) of acceptable purity immediately prior to condensation is the main advantage of the selective activation method, since difficulties associated with the isolation and storage of the reactive monomers may be avoided (III). In contrast to the corresponding amidochlorophosphites (IV), it is also of importance that type (V) compounds are extremely stable and safe to use. From recent studies in this direction the use of bis(dialkylamino)phosphite containing a β-cyanoethyl substituent (V) [$R^1 = CNCH_2CH_2$; $R^2 = R^3 = CH(CH_3)_2$] is noteworthy.[30]

A somewhat different approach has been suggested by Korean workers[33] for the use of diamidophosphites (V). The method recommended resembles previously-described techniques for two-stage phosphite condensation.[31,32]



In this case (V) is initially activated with an equimolar quantity of tetrazole, and the nucleoside component attached to the solid phase reacts with the protected compound (I) in solution even in the presence of excess tetrazole. However the active component in the phosphite synthesis, the phosphoramidite, is irreversibly inactivated by traces of water. Therefore, like the early methods, the main defect of this method[33] is that this active component is associated with the polymer and it is impossible to maintain an excess of this component.

Recently yet another modification has been proposed for the synthesis of phosphoramidites (III) which is based on selective activation:[34]



The phosphorylating agent, bis(diisopropylamino)chlorophosphine, is quite stable and may be purified by vacuum distillation. The intermediate nucleoside bis(diisopropylamido)phosphite subsequently reacts with an alcohol R'OH to yield the required phosphoramidite (III). This variant has none of the limitations associated with the problems in obtaining dichlorophosphites or dialkylamidochlorophosphites.

A stage in which the preparation is obtained in the form of a dry powder by re-precipitation or directly from the reaction mixture or after chromatography in a silica gel column is quite typical for most above-mentioned modifications used for synthesis of nucleoside phosphoramidites (III). This is an extremely important stage in regard to the purity of the compounds (III) obtained and consequently their stability. The purity of phosphoramidites can be most conveniently monitored according to ^{31}P NMR spectra and in certain cases by thin-layer chromatography.[17] The use of fast atom bombardment mass spectrometry has been proposed for this purpose. This technique permits the detection of molecules of phosphorus-free impurities.[35] However the question arises of whether it is absolutely essential to obtain dry and extremely pure phosphoramidites (III) for satisfactory long-term storage and further use in the synthesis of oligonucleotides. In an earlier study[36] phosphoramidites (III) were prepared by a very conventional method, which involved the interaction between an equimolar ratio of nucleosides (I) and amidochlorophosphite (IV) [$R^1=R^2=R^3=CH_3$] in the presence of the base, ethyldiisopropylamine. After removal of the base as the hydrochloride and replacement of the solvent (tetrahydrofuran by actonitrile) the phosphoramidite (III) solutions were used for solid-phase synthesis of oligonucleotides. Preparations of morpholidophosphites (III) [$R^1=CH_3$, $R^2R^3=(CH_2CH_2)_2O$] obtained by a similar method were even more stable, and after storage for many months they were used for the synthesis of oligonucleotides of differing length up to 52 bases.[37]

2. The Effect of the Protecting Group at the Phosphorus Atom and the Nature of the Original Amine on the Properties of the Nucleoside Phosphoramidites (III)

Historically the first acid used in phosphoramidite synthesis was dimethylaniline hydrochloride, which on interaction with phosphite (III) [$R^1=R^2=R^3=CH_3$] quantitatively (according to ^{31}P NMR data) generated the corresponding nucleoside chlorophosphite (II).[10] Both the nature of the substituents R^1, R^2 and R^3 and also the acidity of the selected activator should naturally have an effect on the rate at which the reaction occurs. From the practical viewpoint phosphoramidites (III) with more electron-accepting substituents at the P atom are more stable during the isolation procedure and storage and they require stronger proton donors for activation. Compounds (III) with more lipophylic and bulky substituents at the N atom are also found to be more stable. When the R^1, R^2, and R^3 substituents are selected, any potential difficulties in the preparation of the respective phosphorylating agents (IV) should be taken into account or alternative routes for synthesis of the phosphoramidites (III) should be considered. The main criterion for selection of the R^1 substituent should be the ease with which it can be removed and the selectivity of the removal process following oligonucleotide synthesis.

Table 2. Certain phosphoramidites (III) used in the synthesis of oligonucelotides.

R^1	$-NR^2R^3$	Method of activation (solvent, activation period, min)	Refs.
CH_3-		5-*p*-nitrophenyltetrazole (acetonitrile, 1-3)	[38]
		tetrazole (acetonitrile, 10)	[39]
		oxybenzotriazol(tetrahydrofuran, 3)	[25]
CH_3-	$-N(CH_3)_2$	tetrazole (acetonitrile, 5)	[36]
CH_3-	$-N[CH(CH_3)_2]_2$	tetrazole (acetonitrile, 5)	[40]
$C_6H_5SO_2CH_2CH_2$	$-N(CH_3)_2$	tetrazole (acetonitrile, 10)	[23]
$CH_3SO_2CH_2CH_2$		oxybenzotriazole (tetrahydrofuran, 3)	[13]
$NCCH_2CH_2-$	$-N[CH(CH_3)_2]_2$	5-*p*-nitrophenyltetrazole (acetonitrile, 5)	[16]
		N-methylaniline trifluoroacetate (acetonitrile, 5)	[21]

Certain known and currently used monomers (III) are presented in Table 2. It should be noted that one can only speculate on the possible advantages of certain specific phosphoramidites (III) over others. These assessments, which are based on yield comparisons at the condensation stages, final oligonucleotide yields, and certain other criteria, may not necessarily take into account the diversity of the condensation conditions, the properties of the solid-phase supports used, the apparatus, and the authors' individual interpretations. Nevertheless, as a result of the findings of many research groups the diisopropyl phosphoramidites (III) [$R^1=CH_3$, $R^2=R^3=CH(CH_3)_2$] [11,40] and morpholidophosphites (III) [$R^1=CH_3$, $R^2R^3=(CH_2CH_2)_2O$] [11,15,17] can be currently regarded as the most important agents practically. The former compounds are extremely stable and may be obtained in an appropriately pure form by direct precipitation in hexane without the use of chromatography, and they are therefore commercially most readily available. The latter compounds have even higher stability and may be carefully purified by means of silica gel chromatograpy. The methyl group in oligonucleotides, which have been obtained by using these phosphoramidites (III) [$R^1=CH_3$], may be easily removed by triethylammonium thiophenolate. However, a number of research groups use alternative protecting groups, which may be removed by the β-elimination mechanism under conditions in which the oligonucleotides are completely deblocked (concentrated aqueous ammonia, 50 °C): cyanoethyl [$R^1=NCCH_2CH_2$],[16] methylsulphonylethyl [$R^1=CH_2.CH_2SO_2CH_3$],[13] and phenylsulphonylethyl [$R^1=CH_2CH_2SO_2C_6.H_5$].[23] Monomers containing the cyanoethyl group are also commercially available. Apart from the absence of a separate stage for

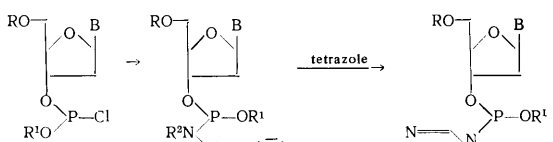
removal of the protecting group R after synthesis of the oligonucleotides, when these agents are used the obnoxious compound, thiophenol, may be omitted. Certain authors question the use of the cyanoethyl group and note that it is unstable in the presence of bases used when unreacted hydroxyl groups on the support are blocked.[5]

o-Chlorophenyl protection could be a possible alternative.[20,21] These phosphoramidites (III) [$R^1 = C_6H_4Cl$] are even more stable than their methyl analogues (III) [$R^1 = CH_3$, $R^2R^3 = (CH_2CH_2)_2O$] and may be readily purified in short columns of silica gel. In this case a five-fold excess of phosphoramidite over the nucleoside component in the polymer has been found adequate for oligonucleotide chain elongation in solid-phase synthesis, whereas in all other studies a 10–20-fold excess of phosphoramidites (III) with $R^1 = CH_3$ has been used.[21] The *o*-chlorophenyl protection can be quantitatively removed by tetramethylguanidinium *p*-nitrobenzaldoximate, but this procedure is much more time-consuming than treatment with thiophenolate and requires subsequent gel-filtration of the deblocked sample.

Phosphoramidites (III) containing a 1,1-dimethyl-2,2,2-trichlorethyl protecting group [$R^1 = C(CH_3)_2CCl_3$] have also been proposed, and the latter may be removed under reducing conditions, for example with tributyl phosphine or zinc dust.[41] This group has previously been used in the chlorophosphite approach.[9]

3. Amidophosphites (III) of Especial Interest

Immobilisation of the protected nucleoside chlorophosphite (II) on polystyrene containing NH-groups has effectively resolved the problem of isolating the required phosphoramidite (III).[42] After this type of polymer had been washed with tetrazole in acetonitrile, a solution of the nucleoside phosphite tetrazolide was obtained, and the latter may be effectively used in solid-phase synthesis.

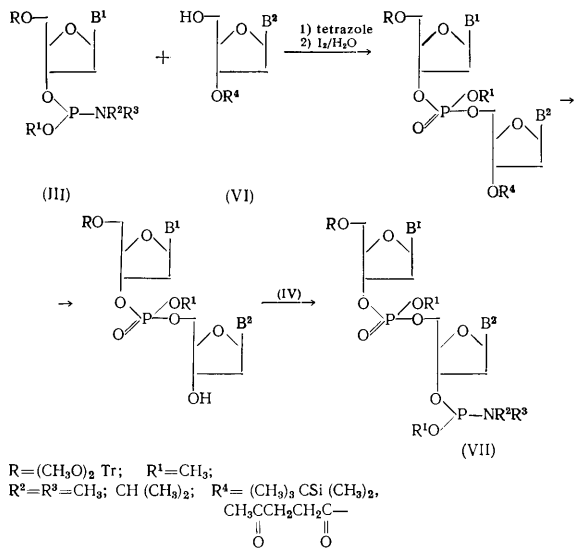


This original scheme would probably be most useful in a study of the mechanisms of phosphite (III) activation rather than from a practical standpoint.

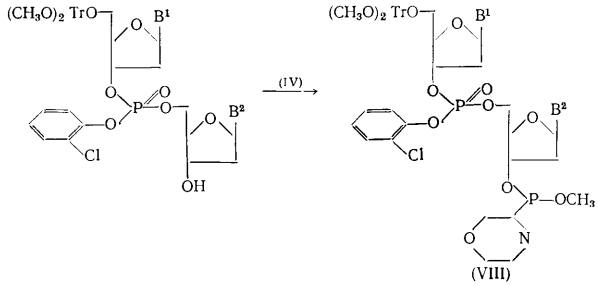
Even in the initial stages in the elaboration of the phosphite synthesis it was suggested that the synthesis should be performed by protecting the exocyclic amino groups in the heterocyclic rings.[43] The development of this concept as applied to the phosphoramidite variant led to the formation of phosphites (III) in which the bases had unprotected amino groups and also to the synthesis of certain dimers based on these phosphites.[22] Speed and cost efficiency are the attractions of this strategy. However it is inconsistent with the trend in solid-phase synthesis in accordance with which protection of amino and hydroxyl groups in the heterocyclic ring is becoming more reliable and perfected, and even in the distant future it is unlikely that this method could be used for preparing oligonucleotides of significant length. Some authors[22] consider that the principle of minimal protection could be useful in the synthesis of many short oligomers on cellulose discs.

4. Phosphoramidite Dimer Blocks

For some considerable time the use of pre-formed blocks in oligonucleotide synthesis monopolised conventional triester strategy. It appeared that during use of the monomers (III), on account of the speed and high yield of the phosphite condensation, any desired result could be achieved. However, a number of papers have now been published which describe the use of dimer blocks in phosphite synthesis.[9,44–49] There is normally a phosphate internucleotide linkage in such dimers which differs only in regard to the method employed for creating this bond (the latter may be both phosphotriester and phosphite and may be subsequently oxidised to phosphate). For example in a previous study[44] phosphoramidite blocks may be obtained as follows:



The levulinic protecting group R^4 was used which may be removed by mild hydrazinolysis. In the case of cytosine derivatives the use of (VI) containing the levulinic group is complicated by the poor solubility of this type of component in virtually any convenient solvent. This problem is resolved by substitution of levulinic by butyldimethylsilyl protecting groups. The resultant dimers are precipitated with cold hexane and may be stored until required. By using such dimers a number of oligonucleotides 29 bases in length have been synthesised. Other workers[45] have used pre-formed nucleoside blocks containing *o*-chlorophenyl protection of the internucleotide phosphate obtained by the normal triester method. By phosphorylation of these preparations it has been possible to construct 16 dimer blocks (VIII):



The blocks were purified by column chromatography and were characterised with the aid of ^{31}P NMR spectra.

The present authors consider that the above-mentioned methods for preparing phosphoramidite dimers require approximately the same number of man hours, and the choice of tactics has evidently depended on which method of synthesis in solution (phosphate or phosphite) the research worker has more effectively elaborated. However, since there were two different protective groups on the phosphorus in oligonucleotides synthesised with dimers (VIII), two different deblocking procedures should be carried out.

The use of phosphite blocks is undoubtedly accompanied by an increase in the yield of synthesised oligomers, since in this case there is a decrease in the number of essential condensations and secondary reactions are also reduced. The most outstanding example of the use of this method has been the synthesis of a 101-base polynucleotide.[48] However, construction of the blocks is a laborious process which demands very highly qualified personnel, and it is unlikely that phosphite dimers will be used extensively in practice for solid-phase synthesis. Increases in yield of oligonucleotides may apparently be achieved by less expensive methods, for example by scale-down of the process, by increasing the concentration of the monomeric phosphoramidites (III), and by optimising the solid-phase cycle with the aim of minimising secondary reactions.

III. REACTIONS AND REAGENTS FOR SOLID-PHASE PHOSPHITE TRIESTER SYNTHESIS

The main aspects of the solid-phase phosphite synthetic cycle are well conserved and comprise a sequence of stages including detritylation, condensation of nucleoside and nucleotide components, oxidation of phosphite to phosphate, and blocking of unreacted hydroxyl groups. However, the duration of the complete cycle has been reduced from 30–60 minutes to 10 minutes or less over a five-year period by the modern automatic synthesisers. This more rapid cycle time has resulted from the shortening of non-productive time in the automated devices, improvements in the mass-transfer processes as a consequence of solid-phase supports, and also the selection of the most appropriate reactions and reagents for rapid synthesis.

1. Detritylation and 5′-Protecting Groups in Phosphite Synthesis

The dimethoxytrityl group is often used for protection of the 5′-position of nucleotides in the phosphite synthesis. Similar types of groups may be removed in acid solution and in principle they may be accompanied by cleavage of purine bases. There is a large amount of data on the actual effect of depurination on the composition of the final reaction mixtures but these data are inconsistent.[6,50–55] It has been reported that removal of the dimethoxytrityl group under normal conditions (3% trichloracetic acid in dichlorethane) is not accompanied by any noticeable depurination throughout the treatment period (1.5 minutes per cycle).[54,55] Nevertheless certain authors as mentioned above prefer to use zinc bromide in nitromethane as a slowly acting but extremely selective detritylating agent.[45,46]

The monomethoxytrityl group is even more inconvenient for solid-phase synthesis if one considers the suggestion that secondary reactions may occur during detritylation. However there is an experiment cited in the literature in which this group has been effectively employed in phosphoramidite synthesis.[56] Various alternative detritylating solutions have been proposed by means of which the monomethoxytrityl group can be removed in the solid phase as rapidly as the dimethoxytrityl group: 0.1 M trifluoroacetic acid in dichloromethane, 1 minute;[56] 5% trichloroacetic acid in dichlorethane, 3.5 minutes,[57] 1 M $ZnBr_2$, 0.02 M 1,2,4-triazole in a dichloromethane-isopropanol mixture (85:15), 1.5–3 minutes.[58]

In a previous study[59] a number of triphenylcarbinol derivatives has been examined and different protecting groups have been proposed for each of the four nucleosides. Under normal detritylation conditions these groups give solutions of triarylmethyl cations in different colours (orange, blue, red, and black) and it is thus usually possible to monitor the sequence of bases in the oligomer under synthesis.

In principle weak acids used for promoting phosphoramidites may also have a detritylation action. Thus apparently the 9*H*-9-phenylxanthenyl (pixyl) protecting group, being more acid-labile than the dimethoxytrityl group[60] has not gained popularity among those who favour phosphite synthesis. The proposed protecting groups for the 5′-terminus in phosphite synthesis do not only consist of derivatives of triarylmethanes. The alkali-labile *p*-phenylazophenyloxycarbonyl group[61] has recently been reported, although at present difficulties would be encountered in the extensive use of this grouping.

2. Blocking of Unreacted Hydroxyl Groups on the Support (Capping)

As with detritylation, at this stage there are no major differences in any of the modifications of the solid-phase synthesis. In the early studies this stage was carried out by using phenyl isocyanate[7] or diethyl chlorophosphite.[8] The use of mixtures based on acetic anhydride in pyridine, lutidine, or collidine[46] is currently preferred, since they are more convenient in practice and quite effective, especially in the presence of the nucleophilic catalysts, dimethylaminopyridine[13,25,55] and N-methylimidazole.[56] This stage is essential for the synthesis of extended sequences, since it facilitates markedly subsequent isolation of the required oligonucleotides. It has already been mentioned in Section II that under certain conditions capping may lead to undesirable secondary reactions.[5]

3. Phosphoramidite Condensation and Factors Affecting the Efficiency of the Condensation

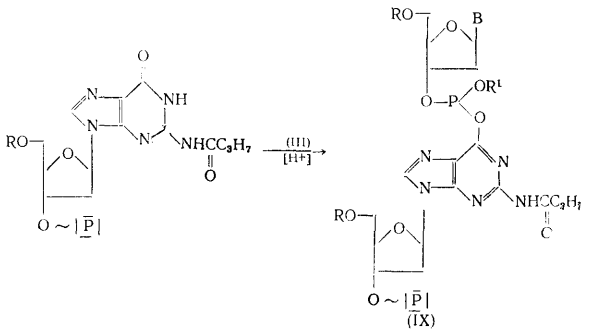
This stage is most important in regard to the efficiency of solid-phase synthesis. Acid activation of phosphoramidites has been briefly discussed by the present authors in Section II. In this Section weak acids normally used for this purpose are presented (Table 2). Tetrazole is most frequently used and may be obtained in a suitably pure and dry form by vacuum sublimation of commercially available preparations. However, tetrazole is not suitable when using the more stable type (III) compounds, for example the morpholidophosphites (III) [$R^2R^3=(CH_2CH_2)_2O$], and more effective proton donors are used in such cases. Selection of an acid should be made on the basis of the following properties: a) high stability in the medium; b) ability to protonate the selected phosphoramidite (III) at a rate compatible with the practical conditions; c) the absence of any detectable deblocking of the nucleotide component under the condensation conditions; d) chemical stability of the working acid solution for the entire duration of oligomer synthesis.

A distinctive feature of phosphite synthesis is the large (10–20-fold) excess of reagent (III) over the nucleoside component in the polymer. This excess is essential not only for ensuring an adequate rate of reaction for chain elongation but also for compensating the

consumption of phosphite (III) in secondary reactions, for example with the residual moisture in the solvents (in the phosphotriester condensation in the traditional variants an excess of condensing agent fulfils this function). However, in work involving micro-scale solid-phase synthesis even these excess quantities are found to be acceptable, and in certain instances authors have changed the method by repeating each condensation twice, and this modification guarantees that the process will proceed quantitatively.[28,48,62]

A significant excess of phosphite is undoubtedly an essential prerequisite for a highly efficient condensation. However, is this condition sufficient? A completely negative answer has been given to this question, viz. steric factors play a key role on solid-phase supports with a high degree of nucleoside modification.[62] It has been established empirically that an extremely high yield on silica supports is ensured, when the nucleoside loading does not exceed 0.4 $\mu mol/m^2$. The currently extensively used solid-phase supports based on glass modified with long-chain aminoalkyl "spacers" in particular satisfy this condition. It is relevant that the authors are aware of only one study in which phosphoramidites (III) have been used for the synthesis of cellulose discs.[65] The difficulties associated with mass-exchange on the cellulose matrix outweigh the main advantage of phosphite synthesis, viz. speed, and compound the problems associated with secondary reactions.

Secondary reactions can play an important role in reducing the yield at the condensation stage. For example, it has been shown that guanidine may be phosphorylated at position O(6) with the formation of "pseudo" chains, which are subsequently destroyed on treatment with aqueous ammonia:[54,55,66]



This process may to a marked extent complicate the synthesis and subsequent isolation of oligonucleotides with a high guanosine content. Difficulties may be avoided by the use of phosphoramidites (III) comprising O(6)-*p*-nitrophenylethyl-protected guanosine derivatives[54,55] or β-cyanoethyl group.[68] However, data are available which indicate that on introduction of a bulky diphenylcarbamoyl goup at this position there is a decrease in the rate of condensation due to steric hindrance.[67]

The product formed by phosphorylation at the heterocyclic ring (IX) is sufficiently reactive to be attacked rapidly by certain nucleophiles. This approach is the basis of a number of techniques for the decomposition of compound (IX) immediately after the condensation before oxidation to the phosphate, which markedly increases the possibility of synthesising oligonucleotides with a high guanosine content.

1) Regeneration of guanosine with water or the acetate ion before oxidation with iodine; the regeneration process also takes place, when a mixture of acetic anhydride and pyridine is used for capping prior to oxidation;[68]

2) the use of N-methylalanine as a phosphoramidite (III) activator;[68]

3) oxidation with an iodine solution in a pyridine-acetic acid mixture; in this case the product (IX) is attacked by the acetate ion more rapidly than oxidation of phosphite to phosphate.[56]

The instability of phosphoramidite derivatives of guanosine in solution during storage was the object of a thorough investigation in an earlier report.[69] This instability presents certain difficulties in the synthesis of mixed oligonucleotide probes, since the mixture becomes depleted of oligonucleotides with a high guanosine content. With the aid of ^{31}P NMR spectroscopy it was shown that a substance with a chemical shift corresponding to a secondary phosphate is predominant among the phosphoramidite (III) degradation products. The mechanism of this process has not been precisely determined, but there are grounds for suggesting that products from the type (IX) phosphorylation are formed as intermediates. These authors[69] also note that in the case of phosphoramidites containing a cyanoethyl group (III) [$R^1 = CH_2.CH_2CN$] the guanosine derivatives are not as unstable as the methyl analogues (III) [$R^1 = CH_3$].

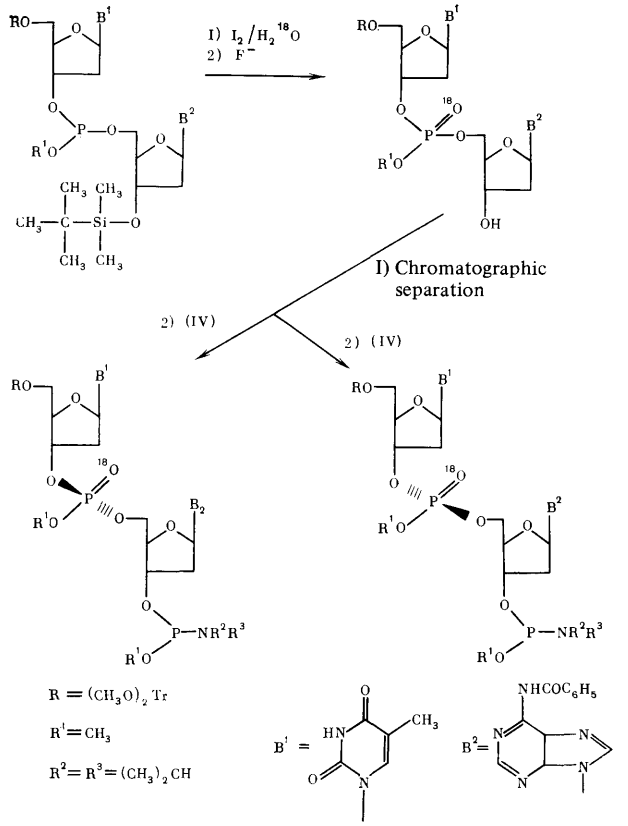
With phosphoramidites (III) [$R^1 = CH_3$] methylation of the thymine heterocycle may also occur,[70] although the practical importance of this type of secondary reaction under the actual conditions of solid-phase synthesis is questionable.[5] On the whole the effect of secondary reactions on oligonucleotide synthesis is clearly illustrated by the following example. When extended products from automatic phosphoramidite synthesis (60–90 bases) are cloned, on average there are base substitutions or deletions in 40% of the clones.[71]

4. Oxidation

This process is traditionally achieved with the aid of iodine in an aqueous-organic solution. The reaction is rapid and selective, although alternation of treatment of the support with water when the latter possesses a certain sorption capacity with subsequent condensation in "absolute" solution cannot be regarded as a satisfactory procedure. In an earlier study[6] *m*-chloroperbenzoic acid in pyridine was used as the oxidising agent, although this agent rapidly lost activity in the course of the synthesis. Currently bis-trimethylsilyl peroxide[72] is recommended for the conversion of phosphite to phosphate in the solid phase including the trimethylsilyl ester of pertrifluoromethane sulphonic acid as catalyst,[73] tetrabutylammonium periodate,[74] and iodosobenzene diacetate.[74] The latter compound is of interest, since it may be used directly in the capping solution. In regard to their application to solid-phase synthesis the new reagents are still under investigation although extensive testing of these compounds will be restricted by their lower availability in comparison with iodine. Nevertheless taking into account the modern-day arsenal of oxidising agents one would anticipate that new studies in this direction will be performed. The use of iodine in a pyridine-acetic acid mixture is also a promising method.[56]

The oxidation stage or generally the transition from tricoordinated phosphorus derivatives to tetracoordinated phosphorus derivatives is of great significance for the synthesis of oligomers modified at the internucleotide linkage. It has been shown that during condensation in the presence of phosphoramidites (III) phosphite triester

enantiomers are obtained, and that the ratio of the latter is dependent on the reaction conditions.[45,75,76] If $H_2{}^{18}O$ is used for the oxidation with iodine, the corresponding isotopically chiral phosphates are obtained and they may be used for the synthesis of chiral blocks.[47]



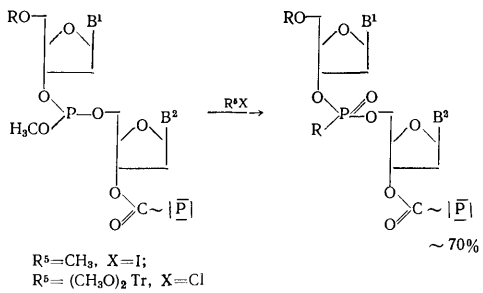
Both of these blocks are further used for the synthesis of oligonucleotides, which differ only in regard to the configuration of one of the internucleotide phosphates.

The phosphite synthesis is extremely convenient for the preparation of thiophosphate analogues of oligonucleotides, which are often used as model compounds in enzyme studies (see communication[77] and the references cited in this article for recent studies on the use of these analogues). In the automated solid-phase method of Stec et al.[78] the thiophosphate bond was introduced at the "oxidation" stage, aqueous iodine having been replaced by sulphur (0.4 M S_8 in lutidine; 60 °C; 15 minutes). The resultant chiral oligomers with respect to thiophosphate in most cases could be separated chromatographically into the individual enantiomers.

In a similar way to the thiophosphates, selenium phosphate analogues could in principle be obtained, the latter compounds being of interest in regard to X-ray structural studies on DNA and for studies on $^{31}P-{}^{77}Se$ spin–spin interactions. However, the authors[78,79] were only able to obtain a few di- and tri-nucleotide analogues (0.1 M KSeCN in acetonitrile; 60 °C; one hour), since selenium is lost by some mechanism unknown to the investigators during the repeating cycles at the stage involving oxidation with iodine.

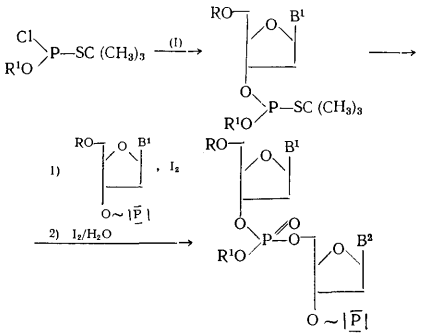
In the interaction between trialkylphosphite intermediates in solid phase and an iodine/alanine/lutidine mixture several phosphoramidite analogues of di- and trinucleotides were obtained, although the yield of the required products was low (less than 20%) and the methodology is in need of development.[79]

The internucleotide linkage may also be modifed by using the Arbuzov rearrangement.[80]



Oligomers obtained by means of this technique, in which one or several internucleotide groupings are phosphonate, may also be separated into the individual enantiomers with the aid of reversed-phase high performance liquid chromatography.

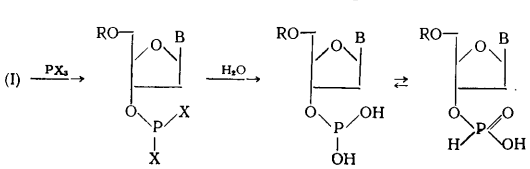
A new modification of the phosphite synthesis has been proposed in which the oxidation and condensation stages may essentially be integrated. Thiolphosphites[81] are used as the original monomers in this method:



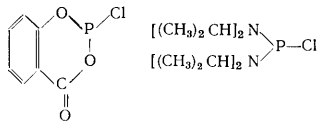
The condensation is achieved in the presence of iodine in an anhydrous solvent, and oxidation may be subsequently carried out by simply adding water. However, it is unlikely that in the near future this method will provide a realistic alternative to the well developed phosphoramidite condensation.

IV. NUCLEOSIDE PHOSPHITES IN THE SYNTHESIS OF OLIGONUCLEOTIDES (PHOSPHONATE SYNTHESIS)

It has recently been proposed that nucleoside phosphites (X) mainly in the H-phosphonate form should be used as monomers in solid-phase synthesis. The procedure used for synthesis of oligonucleotides is known as the "phosphonate" method.[82–85] The methods for preparing nucleoside phosphites (X) proposed by the pioneers of solid-phase phosphonate synthesis are based on the interaction between nucleosides (I) and tris(azolyl)phosphines:



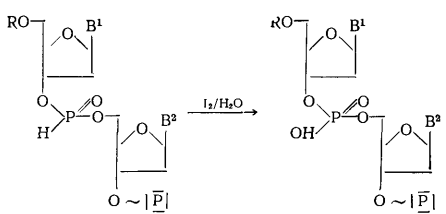
Naturally, in order to prevent the formation of di- and tri-esters of phosphorus acid, a great excess of these phosphorylating agents was used. Later a report was published on the use of other phosphorylating agents:[86]



The use of these agents reduces the possibility that by-products are formed instead of tris(azolyl)phosphines. In all cases[82–86] monomers (X) obtained as a result of phosphorylation and subsequent hydrolysis were purified with the aid of adsorption or reversed-phase column chromatography. The nucleoside phosphites (X) are sufficiently stable in the form of tertiary amine salts and may be stored for considerable periods.

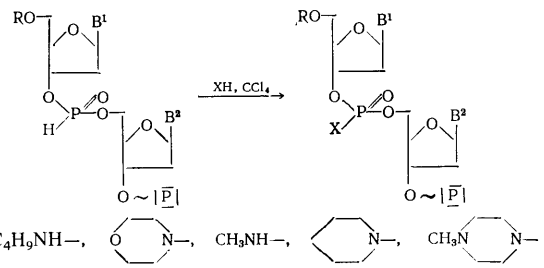
It has been shown that various anhydrides and acid chlorides of phosphorous acids and carboxylic and sulphonic acids may serve as monomer (X) activators during oligonucleotide synthesis, although the acid chloride of trimethyl acetic acid was found to be the best of the agents tested.[84,85] It has been suggested that the active phosphorylating compound in this case is a mixed anhydride of phosphorous and carboxylic acids. It is considered that pre-mixing of the nucleoside phosphite (X) and pivaloyl chloride leads to the formation of a bifunctional phosphorylating agent, diacyl nucleoside phosphite. It is therefore recommended that the reagents should be mixed directly during the condensation process in the reactor.[85]

A separate capping stage is evidently not required in the phosphonate synthesis, since non-phosphorylated hydroxyl groups on the support should be acylated in the condensation process. As there is a five-fold excess of condensing agent (pivaloyl chloride) over monomer (X), in the phosphonate method a lower amount of nucleotide component is consumed than in the phosphoramidite method. The internucleotide phosphite diester groups formed during the synthesis are chemically quite inert and do not require protection. They are oxidised with iodine in an aqueous-organic solution at the end of oligomer synthesis.



However the oxidation process is slower than with the trialkyl phosphites and in order to promote the oxidation, catalysis with stronger bases than pyridine is necessary.[84] Thus in the phosphonate synthesis the chain elongation cycle consists essentially of a condensation stage (1–2 minutes), detritylation (1–2 minutes), and a washing procedure, and therefore greatly extended oligonucleotides containing up to 100 bases may be synthesised rapidly.[84] At present there are certain unknown factors and reservations in regard to this synthesis. For example, partial detritylation in the condensation process[84] or incomplete capping is thought to occur. However, the phosphonate method is extremely straightforward and cost effective, and very shortly many research workers will undoubtedly favour this method.

This method also shows promise in regard to the synthesis of oligonucleotide analogues. Unfortunately the phosphite diester group itself is unstable in the presence of bases, and an unoxidised oligomer containing phosphite diester internucleotide groups cannot be removed from the support by conventional methods. However, this group may be susceptible to attack by a nucleophile, for example the Atherton–Todd reaction. This property has been exploited by Gryaznov et al.[87] for the synthesis of dinucleotides containing an internucleotide phosphamide linkage. By the application of this reaction to the oligomeric product from the solid-phase phosphonate synthesis it has been possible to obtain a number of amidophosphate analogues of oligonucleotides:[88]



This communication[88] describes the synthesis of nine undecathymidylate analogues which contained different numbers of morpholidophosphate internucleotide groups, and also mentions the possibility of preparing thiophosphate [0.1 M S_8 in a triethylamine–carbon disulphide (1:9) mixture 5 min] and triester [10% alcohol in an N-methylimidazole–triethylamine–carbon tetrachloride (5:5:90) mixture] analogues of oligonucleotides via the phosphite diesters on a support.

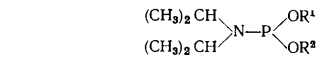
V. PHOSPHITE REAGENTS FOR THE INTRODUCTION OF DIFFERENT FUNCTIONAL GROUPS INTO OLIGONUCLEOTIDES

Oligonucleotides are nowadays increasingly used as carriers for various groupings, for example chemically active (complementarily addressed modification) and reporter (nonradioactive probes) groups. Research workers are focusing attention on the replacement of a number of enzyme processes in genetic engineering (for example kination and ligation) by purely chemical processes. There would be strong grounds to use for such purposes the same chemical arsenal as for the synthesis of the oligomers themselves.

1. Introduction of the Phosphate Group at the 5′-Terminus of the Oligonucleotide

This operation represents a chemical alternative to the kinase reaction and has been thoroughly worked out in the phosphotriester synthesis. The main problem associated with the introduction of the 5′-terminal phosphate is the selection of a phosphorylating agent with easily removable protecting groups at the phosphorus atom, confirmation that the phosphorylation has taken place, and also the separation of the 5′-phosphorylated oligonucleotide from the normal oligonucleotide (when the chain is long enough, there is an insignificant difference between the chromatographic and electrophoretic mobility of both oligomers).

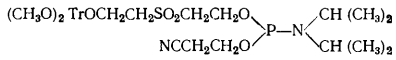
Several phosphorylating agents prepared by conventional methods of phosphite synthesis have been proposed.[89,90]



$R^1=R^2=CH_2CH_2C_6H_4NO_2$; $R^1=R^2=CH_2CH_2CN$;
$R^1=CH_3$, $R^2=CH_2CH_2C_6H_4NO_2$; $R^1=CH_3$, $R^2=CH_2CH_2CN$

Solid-phase phosphorylation of the oligomers by such agents with the aid of acid catalysis, oxidation, and subsequent deblocking yields the required oligonucleotide-5'-phosphates. Methyl and β-cyanoethyl groups are accordingly removed before the support is treated with ammonia and during this treatment. The *p*-nitrophenylethyl protection may be removed only by strong bases such as diazabicycloundecene. It may therefore be used as an hydrophobic probe during the removal of the 5'-phosphate of the oligomer by reversed-phase chromatography.

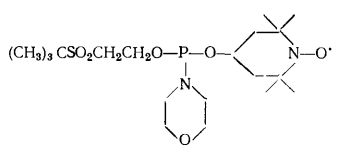
A phosphorylating agent containing the dimethoxytrityl group has also been described:[91]



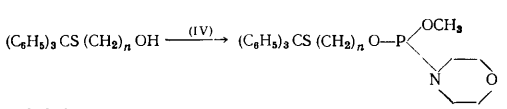
After oxidation of the phosphorylated oligomer and treatment with acid it is possible to determine whether phosphorylation is complete according to the concentration of the dimethoxytrityl cation. The remaining ethoxysulphonylethyl fragment is removed together with the β-cyanoethyl protection when the support is treated with ammonia.[91]

2. Introduction of the Reporter and Functional Groups

The synthesis of a phosphoramidite containing a nitroxyl fragment is an example of the direct introduction of a reporter group with the aid of a phosphorylating agent:[92]



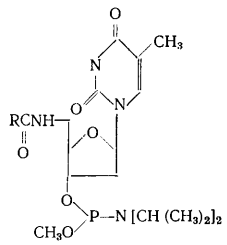
However, reporter groups such as coloured or fluorescent chromophores are often complex in structure. It is easier to introduce these groups under milder conditions into oligonucleotides, which have been preliminarily modified with certain functional groups. The authors of a study on 5'-phosphorylation with the aid of phosphoramidites[89-91] note that by using phosphite reagents it is possible to introduce a 5'-terminal thiophosphate, a potential acceptor group for different modifiers. A morpholidophosphite with trityl protection has been used to introduce the thiol group:[93]

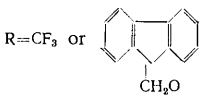


$n=2, 3, 6$

After phosphorylation of the oligonucleotide and oxidation with iodine the trityl group was removed with silver nitrate.

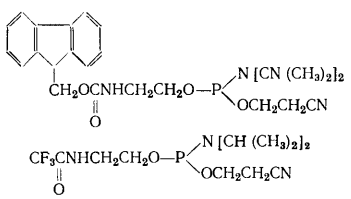
The amino group was introduced by means of phosphoramidite derivatives of 5'-deoxy-5'-aminothymidine:[94]





Alkali-labile groups (fluorenylmethoxycarbonyl or trifluoracetyl) were removed while the support was being treated with ammonia. Oligomers containing amino groups obtained in this way have been used in the synthesis of primers for sequencing according to the method of Sanger which carried a fluorescent marker at the 5'-terminus.[94]

The fluorenylmethoxycarbonyl[95] and trifluoracetyl[96] groups have also been used in the construction of other phosphorylating agents, in order to introduce the amino group.



In the latter case in order to increase the yield of the required oligonucleotides, the protecting groups were removed not with ammonia but with diazabicycloundecane.[96]

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As a result of the development of methods for nucleophilic catalysis it is now possible to achieve a phosphotriester condensation quite rapidly and efficiently.[67,97-101]. However, commercial manufacture of nucleoside phosphoramidites and automatic synthesisers, which operate according to the phosphoramidite cycle, has indeed become a mass-production venture. Phosphonate synthesis is also being rapidly commercialised. Operations in the synthetic cycle are constantly being improved and simplified with the result that the chemical synthesis of DNA is a rapidly-developing and refined procedure. The demand for modified oligonucleotides is also attracting increasing attention in regard to nucleoside phosphites and fundamental questions on the chemistry of organophosphorus compound, which should ensure further advances in phosphite synthesis.

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Future Outlook for the Construction of Biologically Active Compounds

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The state of the art in regard to studies on the relation between structure and properties expressed by chemical compounds, especially biological activity, has been assessed, the determination of structure-activity relationships being the only feasible alternative to costly empirical screening. It has been shown that in this area of research, which embraces the fields of chemistry, physics, mathematics, and biology, further advances will only be possible by means of a compatible language for the computer-aided description of structure, and methods for revealing structure-property relationships and quantitative criteria of properties.

CONTENTS

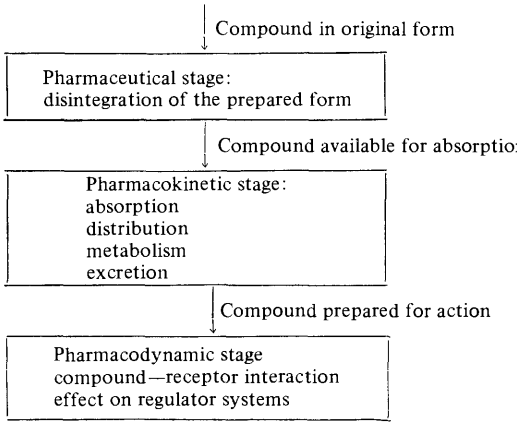
I. Introduction 897
II. Molecular recognition, the platform of the structure-activity relationship 898
III. Correct computer-aided description of structure for establishing a structure-activity relationship 899
IV. Methods for determining structure-activity relationships 901
V. Software packages for determining structure-activity relationships 904
VI. Conclusions 905

I. INTRODUCTION

Progress in science and technology is concomitant with the growth in number of chemical compounds used in industry, agriculture, medicine, and domestic life. On account of the virtually limitless scope for synthesizing new compounds, chemistry ensures a constant improvement in the exploitable properties of available substances. At present there are approximately ten million known chemical compounds. However, together they represent a negligible portion of the inifinite number of total possible compounds. This is especially evident from the data presented in communication.[1] If merely fifty substituents well characterised in organic chemistry are used for substitution in various combinations into seven free positions of naphthalenecarboxylic acid alone, 7.8×10^{12} chemical compounds may be obtained. It clearly follows that there is a high probability that compounds may be synthesized which have markedly superior properties to those of existing chemicals. In this regard the question of what strategies to adopt in order to obtain highly effective compounds in the shortest possible time with minimal effort is of major importance. The use of comprehensive tests for properties (i.e. total screening) in order to find new preparations is a very expensive excercise (with this approach in order to introduce one new compound, 12 000 – 15 000 chemical compounds must be synthesized and thoroughly examined). For this reason it is necessary to elaborate sound principles for the construction of compounds with the desired properties.

According to references 2, 3 the development of concepts on chemical structure was closely linked to the identification of an interrelationship between structure and the properties expressed, initially at the qualitative level[3,4] but subsequently with the discovery of the periodicity of the elements there was a gradual transition to the quantitative determination of structure-activity relationships.[5]

The problem of establishing structure-activity relationships becomes of particular interest and significance in the search for biologically active compounds. Conventional approaches such as isolation of biologically active compounds from natural sources, synthesis of analogues of natural compounds, study of folk medicine, and extensive biological trials cannot keep pace with the rapidly increaseing demand for new preparations. For this reason from the middle of the nineteenth century a new approach to the search for biologically active compounds began to develop, i.e. determination of the relationship between the structure of a compound and the biological activity expressed by the compound (structure-activity relationship). Justification of this approach was demonstrated by the work of Richardson, who for the first time was able to demonstrate qualitatively the relationship between the structure of certain organic compounds and their physiological activity,[6] and also by the studies of Crum-Brown and Fraser, who made the first attempt to construct a mathematical model representing the relationship between structure and activity.[7] The basic principles for establishing quantitative structure-activity relationships have now been defined (see reference[3] for the historical aspects of the determination of structure-activity relationships). The following schematic illustrates current concepts on the mode of action of biologically active compounds based on quantitative structure-activity relationships:[8]



The interrelationship between the structure of a compound and its biological effect following the introduction of the compound into the body becomes specific and fully expressed only at the pharmacodynamic stage. As regards other processes associated with the transformation of compounds, enzyme inhibition, diffusion of compounds in different organs, etc., information (although steadily growing[9]) is sometimes extremely limited and therefore it is difficult

to determine quantitative structure-activity relationships. Thus the problem of the quantitative structure-acitivity relationship is a special case of the structure-property relationship. However, on account of the complexity of the application of the structure-activity relationship to biological specimens, it is necessary to go beyond the traditional framework of the structure-activity problem and to focus attention not only on methods for detecting relationships and on the development of experimental investigations into structure and the form of the description but also on the quantitative determination of biological activity and on the production of a detailed description of the biological processes themselves.

There are currently thousands of publications devoted to anlalyses of quantitative structure-activity relationships. In a specialised journal (Quantitative Structure-Activity relatinships) commenced publication in 1981 in addition to original articles a large number of abstracts of studies on quantitative structure-activity relationships published in other issues including monographs and reviews are cited.[10–20] However, in most cases these studies are either specialised and focus on a single approach or problem (i.e. regression analysis,[18] the use of computers,[19] application of quantitative structure-activity relationships to the analysis of pesticide activity[20]) or mainly concentrate on a description of mathematical methods for analysis of quantitative structure-activity relationships.[16,17]

In the present review emphasis is place on the basic principles of the construction of compounds with desired properties[21,22] which constitute the physicochemical foundation for the determination of quantitative structure-activity relationships. In this case the research worker should have reliable quantitative information on the level of biological activity that the chemicals possess.[18] When the objective is to establish the quantitative structure-activity relationship there is a tendancy to construct a model which describes the interaction between compound and receptor and to use a method for determining the relationship between the correct (within the limits of the method used) representation of the structure of the compound and the activity which it expresses.

II. MOLECULAR RECOGNITION, THE PLATFORM OF THE STRUCTURE-ACTIVITY RELATIONSHIP

It has now become evident that, when the wide range of properties possessed by chemical compounds is analysed, intermolecular interactions with potential partners should be examined. The so-called "problem of recognition in chemistry" is based on a large amount of information which indicates that a particular molecule A_0 (the recogniser) reacts or forms a complex in solution only with one particular moleculer effector B_0 in a mixture of sometimes a very large number of possible effectors B_i.[23–25]

Historically it was the analytical chemist who first encountered the qualitative aspect of recognition in the search for compounds which effectively bind specific ions in multi-component solutions. With advancements in chemistry the problem of recognition has extended into organic and physical chemistry. In this reagard it is relevant to mention the fundamental studies of van't Hoff concerning the development of the principles of the theory of solutions[26] which may be regarded as the transition to a study of the quantitative aspect of recognition. As mentioned in[25], when these processes are described quantitatively, the accuracy of the recognition of chemical compounds increases by an order of magnitude in sequence from the selective donor-acceptor interaction of H-bonding of molecules containing a single electron donor and acceptor centre, and subsequently to the selective complex-formation of metal ions with polydentate ligands, and to selective catalytic reactions and ultimately to enzyme reactions. In the same sequence there is an increase in the size and complexity of the structure of molecules which are involved in the recognition process.

The methods currently adopted to investigate recognition in chemistry usually involve systems of selective complex formation between macrocyclic polyethers and cryptands (see Refs.27, 28]. However, even for these relatively simple compounds complex stability is dependent on many factors, and it is therefore difficult to establish the principles of molecular recognition. It is therefore essential to establish a clear definition of the basic principles involved in the recognition process.

According to[23–25] recognizer A_0 should bind with a particular type of molecule B_0, i.e. with the correct effector from a solution containing N types of molecule: B_0, B_1, B_2 ..., B_{N-1} of random concentration. The number of possible false recognition events is defined as P_f. Then the degree of recognition may be expressed as the number of correct recognitions which is dependent on the total number of possible effects N and the proportion of false recognition P_f.

In the simplest case formation of complex A_0B_i may be represented by the equation:

$$A_0 + B_i \rightleftarrows A_0B_i$$

with a reaction constant of

$$\frac{[A_0B_i]}{[A_0]\,[B_i]} = K_{0i} = \exp(-\Delta G_{0i}/RT);\ i = 0, 1, \ldots, N-1$$

and the number of possible false recognitions P_f will be equal to

$$P_f = \frac{\sum_{i=1}^{N-1} [A_0B_i]}{[A_0B_0] + \sum_{i=1}^{N-1} [A_0B_i]} = \frac{\sum_{i=1}^{N-1} [B_i]\,K_{0i}}{[B_0]\,K_{00} + \sum_{i=1}^{N-1} [B_i]\,K_{0i}},$$

from which it follows that recognition becomes more accurate the greater is the value of the ratio of the correct recognition binding constant to the false recognition binding constant, or the greater the difference between the free energies ($\Delta\Delta G$) of formation of complexes A_0B_i (ΔG_{0i}) and A_0B_0 (ΔG_{00}) respectively:

$$\Delta\Delta G_i = \Delta G_{0i} - \Delta G_{00}.$$

Thus highly specific recognition demands a relatively large difference between the capacity of the recognizer A_0 to interact with the correct effector B_0 and with a false effector. When $\Delta\Delta G$ values are sufficiently high, recognizer A_0 is able to distinguish one effector B_0 from N other effectors B_i. Thus a targeted search for compounds with the desired properties could tend towards the construction of molecules the structure of which ensures maximum binding with the recognizer responsible for the property under investigation.

These aspects of the question of recognition with respect to biological specimens were further developed in studies by Fischer,[29] who by 1894 had already established that spatial compatibility affects the interaction between substrate and enzyme. This formed the basis of the so-called "lock and key" principle or "complementarity principle". This principle has now been changed to the generally-accepted concept that formation of enzyme-substrate complexes, which play an important role in enzyme catalysis, is determined by the fine

structure of active and effective centres and the unique structure of the overall enzyme molecule which ensure high catalytic activity and the specific action of the biocatalyst.[30]

Another important contribution to the development of the structure-activity concept is associated with Hansch, who in the sixties proposed an empirical model for biological activity based on the linear relationship between the free energy of the process under investigation and physicochemical parameters of the compounds. This model is the most widely used instrument in studies concerning optimization of the biological activity of chemical compounds.[1,31]

Development of the ideas of Fischer and Hansch has so far introduced two independent approaches to structure-activity relationship determinations associated with the selection of common structural elements in different compounds with one particular type of activity and with the optimization of biological activity in a homologous series of chemical compounds. It will later be demonstrated that, in order to make a transition to a qualitatively new level of interpretation of the problem of quantitative structure-activity relationships, these approaches should be unified within the same systemic study. Definition of the problem in this manner implies that the structure of the compounds has been adequately determined and correctly described, including the special features of the electron-topographic and conformational structure of the molecules.

III. CORRECT COMPUTER-AIDED DESCRIPTION OF STRUCTURE FOR ESTABLISHING A STRUCTURE-ACTIVITY RELATIONSHIP

Before commencing a study on the relationship between structure and activity, a method for presenting the original data should be selected.[14] A great deal of effort has been devoted to the selection of a system of parameters which may be either determined experimentally or by calculation and which would fully describe the structure. In the present review four main approaches for describing the structure of compounds are considered.

1. Fragment Code for Substructure Superimposition

A fragment code for substructure superimposition (FCSS) was proposed at the beginning of the seventies.[32] In the analysis of chemical structure based on this strategy potentially active centres named "descriptor centres" are identified and atoms containing mobile p- and π-electrons or a full electrostatic charge are related to these centres. They are all heteroatoms, nitrogen, oxygen, sulfur, phosphorus, halogens, and metals, and also rings and pairs of carbon atoms linked by multiple bonds. A detailed list of descriptor centres is presented in Ref.33. Initially for each compound a set of linear descriptors is produced on the basis of the structural formula, and each descriptor is represented by a seven-digit number (two of the numbers were designated to the descriptor code and the chain length. The property of conjugation was represented by one figure, which was unity in the presence of conjugation and zero when there was no conjugation). A calculation of the characteristics of the cyclic fragments when the compounds were coded for analysis of their similarity is presented in Ref.34. FCSS has been found to be useful in statistical studies on the large amount of information available on biologically active compounds. A method was subsequently proposed for coding the structure of a chemical compound by using the descriptor centre concept while retaining the topology of the molecular structure as a single entity in the form of a connection matrix for descriptor centres (CMDC).[33] In this matrix diagonal elements represent descriptor centre codes and non-diagonal elements may represent the distances between respective descriptor centres (in the case of a matrix for descriptor centre geometry) or the number of linkages between them. This approach has been used in a number of studies[16,17] for identifying the common elements in the structures of compounds possessing a specific type of biological activity.

2. Topological and Geometric Descriptor Systems

The advent of systems of topological and geometric descriptors is the natural development of a language for the description of chemical structures. The Wiswesser system has become the most widely used of the line-formula notation methods.[35] However, in view of the limitations inherent to linear coding systems, the main limitation having already been mentioned, nowadays the coding of structures with the aid of a connection matrix with a wide set of molecular descriptors is preferred. The latter include mainly topological descriptors, fragment descriptors, substructure descriptors, connection descriptors, and environment descriptors, etc. They are all designed to obtain a more accurate description of the vicinity of active centres in molecules.[14] As with FCSS, a deficiency of this coding method is that it is not the structure of the chemical compounds but their structural formula which is coded. This method for describing structure may be somewhat improved, if geometric descriptors are used in addition to topological descriptors. Geometric descriptors, which describe the general form and size of the molecules, imparts a three-dimensional structure to the compound diagram. Conformational calculations of equilibrium distances between the active centres by molecular mechanics techniques provide a more complete description of the structure of compounds.[36] However in this case also it is not possible to reveal the electronic properties of the active centres, which determine their ability to undergo intermolecular interaction. This circumstance significantly affects the identification of real interrelationships between the structure of chemical compounds and the activity which they express.

3. Quantum Chemical Methods Used for Describing Structure

Quantum chemical calculations of molecular structures have been used in structure-property relationship determinations since the time when they first appeared, and also at present as a result of progress in computer technology these methods are becoming more widely used in studies on the relationship between structural parameters of molecules and their properties, especially their biological properties.[19,21,37-39]

Currently-available computer programmes cover virtually the entire range of quantum chemical calculations from elementary schemes for the complete neglect of differential overlap (CNDO) to strict non-parametric approaches: CNDO/2, CNDO/BV, CNDO/S, INDO, INDO(S), MINDO/2, MINDO/3, MNDO, VRDDO, and the ab initio STO-39 calculation. However, the attraction of quantum chemical calculations for structure-activity relationship determinations is mainly that the most stable molecular conformations are determined in which the active centres are accessible for interaction with a receptor or that molecular physicochemical characteristics associated with the transport of the compound to the bio-target are evaluated. By transferring the "centre of gravity" of the

quantum chemical calculations to the electronic properties of the molecules, it has been possible to attempt identification (construction) of compounds with the desired properties within essentially new classes of compounds. The above-mentioned approaches do not offer such possibilities.

It is evident that the use of quantum chemical calculations for structure-activity determinations is a promising approach. Further development of computer technology and transition to non-empirical calculations[40] will undoubtedly lead to an increase in the role of quantum chemistry in the determination of structure-property relationships. Nowadays calculation of the electronic structure of large numbers of chemical compounds will be difficult to achieve even with the use of semi-empirical methods, on account of the huge demands on computer time. In this regard it will be necessary to devise a system of calculation which would be relatively simple and also which would effectively provide the correct description of the electronic structure within the limits of structure-activity relationship determinations. An attempt has been made[41] to fill the connection matrix of descriptor centres with a quantum chemical content, which takes into account the electronic structure of the molecules.

However, one should note that quantum chemistry is by no means a natural source of information on the electron-topographical structure of molecules. Moreover, in view of the above-mentioned difficulties, information obtained as a result of quantum chemical calculations is not always sufficiently reliable and accurate. Hence in the future development of methods for determining structure-property interrelationships, in addition to these calculations, physicochemical approaches to structure-activity relationship determinations will be elaborated and such approaches will be directly associated with experimental studies on the physicochemical properties of molecules or their fragments.

4. The Physicochemical Approach to Structure-Activity Relationship Determinations

Extensive use of physicochemical properties in structure-activity relationship determinations began with the studies of Hansch et al.[1,5,31] The complete set of diverse parameters used in calculations according to the Hansch equation have been described.[18,42] All of these parameters may be separated into three groups. The first group includes parameters associated primarily with hydrophobic properties, the logarithm of the partition coefficient ($\log P$), the lipophilicity parameter (π), thin-layer chromatography parameter ($\log K'$), parachor (Pr), molar volume (Vm), molecuar weight (M), logarithm of partition in water ($\log C_{aq}$), partial pressure (p), the Hildebrandt solubility parameter (σ_s^*), molar attraction constant (F_α), entropy constant (σ_s^{**}) and others. The second group includes various induction and resonance constants (σ^*, σ^0, σ^I, σ^R, etc), radical substitution constants (E_R), Swain and Lupton parameters (F, R), polarizability (α), molecular refraction (MR), dipole moment (μ), ionization potential (IP), spectral frequencies (ν), ionization constants (pK_a, pK_b), and other characteristics associated with electronic properties. Finally the third group consists of parameters characterising steric effects of intramolecular interactions, Taft's steric parameters (E_s and E_s^0), van der Waals radii (r_v), molecular binding potential (χ), etc. Although many of the above-mentioned parameters do not reflect in the pure state only hydrophobic, only electronic, or only steric properties, the separation of these parameters is extremely useful, for example in relation to the problem of multi-collinearity in the selection of parameters for a model in accordance with the scheme for the action of biologically active compounds.

Although the Hansch equation has been effectively used on many occasions, one should however emphasise that this approach and various modifications of this approach "operate" only within the narrow range of related compounds. Replacement of only one active centre in the molecule leads to a change in the nature of intermolecular interactions and consequently to the perturbation of previously-established correlations between physicochemical parameters describing the compound and the property expressed. In this regard the previously described approaches in which common structural elements may be selected would seem to be preferable, since a broad range of compounds could be studied. The question consequently arises, can the Hansch approach be extended for analysis of different orders and classes of compounds by combining this approach with other methods of differentiating common structural fragments. This concept described in Ref.43 was realised for the first time in structure-activity determinations in which the following cases were examined. In the traditional descriptor analysis of the similiarity of structures a set of descriptor centres with their classification in terms of the types of atoms and nature of the linkages is used. In an intramolecular environment the boundaries separating the electronic properties of the descriptor centres may become diffuse and this will complicate the separation of activities. It is therefore evident that descriptor centre classification should be based not on the type of atom but on its ability to participate in intramolecular interactions.

The enthalpy of complex formation (ΔH), which is proportional to the free energy (ΔG) of the interaction between molecules containing one electron-donor or acceptor centre, may provide a quantitative measurement of this interaction.[25] A wide range of experimental data on ΔH values has now been obtained by means of which it is possible to predict the thermodynamic properties of a whole variety of donor-acceptor pair combinations, and therefore one might suggest a new classification of the descriptor centres. For this purpose it is necessary either to have experimental data on ΔH values for all possible donor molecules with a given acceptor or to find a system of empirical parameters with the aid of which the ΔH value for the interaction between any donor–acceptor pair may be evaluated. In the first variant (see for example the donor numbers of Gutman[44]) there are significant limitations such as inadequate solubility of certain complexes or the possibility that an irreversible reaction may occur. The second variant has much more potential, and the two equations presented in[45,46] are extensively used for achieving this objective. In the latter modification of the equation[45] the enthalpy of complex formation is expressed as the sum of three paired products of six types of parameter. The formula based on the classification of donor–acceptor interactions and described in report[43] is much simpler.

According to report[46] the enthalpy of complex formation is proportional to the product of two dimensionless values, the i-acid (acceptor P_i) and j-base (donor E_j) factors.

$$\Delta H_{ij} = -\Delta H_{11} P_i E_j, \qquad (1)$$

where H_{11} is a coefficient determined according to a particular standard complex. In the development of this approach[43] a common scale of donor and acceptor factors has been proposed which is constructed on the basis of the following modification of equation (1):

$$\Delta H_{ij} = |\Delta H_{11}| E_i E_j,$$

where $E_i = P_i$. In later studies[21,22,47] not only neutral but also charged donors and acceptors were included in this approach. A descriptor centre classification based on this common scale has been proposed[48] for the analysis of structure-activity relationships. A list of E_i values for 70 extensively used acceptors and E_j values for 230 diverse electron-donor compounds is presented in communication.[22] Even with this relatively small group of data enthalpy values of complex formation may be calculated for more than 16 000 complexes.

From the analysis of a large group of experimental data on complex formation, the relationship may be established between $E_i(E_j)$ values and substitution constants characterising induction effects and the conjugation effect.[49,50] In this approach it was essential to calculate the values for these constants for complex functional groups. In this regard empirical equations have been derived[52,53] which describe the transfer of the induction effect via carbon, oxygen, and sulfur atoms. The creation of an automated system for evaluating $E_i(E_j)$ values should be regarded as the final stage in the introduction of donor–acceptor factors into the actual construction of biologically active compounds. Recently the authors of this review proposed and derived an algorithm on a NORD-10 minicomputer for calculating the value $E_i(E_j)$ with the automatic determination of the Taft constant of complex functional groups according to the structural formula programmed into the computer and the described types of atoms.† The mathematical software was thus created for providing a physicochemical approach to the description and classification of compounds in terms of electronic properties of descriptor centres used for selecting the structural elements responsible for a particular type of biological activity. Clarity and the high content of easily interpreted principles of the classification are features of this approach, and this classification is sufficiently straightforward for widespread use and it is already used at the qualitative level for constructing compounds with the desired properties.[54]

In addition to the correct evaluation of the electronic properties of descriptor centres, of no less importance is the accurate description of the spatial structure of the molecules, taking into account the dynamics of intramolecular motion, tautomeric and conformational transitions, and large- and small-amplitude oscillations. In this case it is evident that inclusion of descriptor centres in the previously-described connection matrix as non-diagonal elements in the values for the number of linkages between the respective descriptor centres is not consistent with current concepts on the spatial structure of molecules. Inclusion of equilibrium distances[17,33] in the connection matrix and the use of moments of inertia and molecular volumes[21] as descriptors is naturally more appropriate, but does not overcome the problem of correctly describing the spatial structure of the molecules. The use of the concept of the spatial structure of a molecule in the form of a radial distribution plot, as practised in gas chromatography, has been proposed[55] as a simple method for describing molecular structure which in general satisfies the requirements of the "ideal" method. An interesting attempt to use an analogous transformation of molecular structure in order to separate tranquilisers and sedatives[56] is noteworthy, and this method was found to be much more effective than the use of fragment descriptors with this material.[57]

The methods described for representing molecular structure reflect to a satisfactory extent the structure of the compounds, when a computer is used for determining structure-activity relationships.‡ Moreover, selection of the form of description of a molecular structure is closely linked with the particular objective of the study (classification of compounds in terms of the type of bio-activity expressed, an information search for related compounds, identification of common structural elements, a quantitative prediction of the order of bioactivity, etc.) and also with the method used for this purpose. From this point of view the question of optimal conformity between the form of description of a structure and the method selected for treatment of the structure information is very important.

IV. METHODS FOR DETERMINING STRUCTURE-ACTIVITY RELATIONSHIPS

The numerous methods available for determining structure-activity relationships can be divided into the following two major groups according to the type of problem in quesion:[21] methods directed towards the optimisation of properties in a series of related compounds and methods designed for the identification of common structural fragments in molecules of chemicals exhibiting a certain type of bio-activity.

1. Optimisation of Properties in a Series of Related Compounds

This group of methods involves the use of different multi-parameter regression models linking the structural parameters of the compounds with their bio-activity.[58–62] The main strategies for processing structural information used in structure-activity determinations for optimising the properties in a series of related compounds are presented in Table 1.

The successful use of the Hansch model described in the previous section has led to the appearance of many generalisations and modifications for "screening" of different sets of physicochemical and structural parameters and regression models. Even as early as the seventies more than 2000 regression dependences had been derived for more than 20 000 chemical compounds,[63] relating hydrophobic, electronic, steric and other properties of substituents to biological activity expressed by the compound. Certain of these relationships were used both for predicting efficacy[64–66] and also for determining the mode of action of biologically active compounds.[18,67] However, many of these, according toHansch,[68] were "astonishingly deformed". They included equations which were unrealistic in the physical sense or ineffective for predicting biological activity but which had high correlation coefficients.

The existence of these equations indicates that the high values of the correlation coefficient R, the square of which is numerically equal to the contribution of the bio-response function variance ($\sigma_y^2 - \sigma^2$) "explained" by the regression dependence

$$R^2 = (\sigma_y^2 - \sigma^2)/\sigma_y^2,$$

where σ_y is the bio-response function variance, and σ is the residual variance, is an essential condition but would not ensure a good

†A.M.Sapegin, O.A.Raevskii, V.V.Chistyakov, and I.V.Martynov, Khim.-farmatsevt. zhurn., 1987, **21**(9), 1098.

‡O.A.Raevsky, QSAR in Drug Des. Toxicology, D.Hadzi et al., (editors), Elsevier, Amsterdam, 1987, p.31.

regression model. This may be attributed to the fact that for a regression analysis there are certain limitations, and that infringement of the latter leads to "mishaps" with regression coefficients,[69] which characterise the contribution of each of the structure parameters of the compound to the bio-activity value.

Table 1. Main Methods for Optimising Properties in a Series of Related Compounds.

Form of analysis	Method of processing information	Field of use	Refs.
Multidimensional statistical	Calculation of the statistical characteristics of the distribution of random values, means, scatters, etc.	Omission of incorrect data and analysis of "rejections"	[72-76]
Multidimensional scaling	Reduction of the scale of multidimensional space with the object of omitting data and variables which do not provide sufficiently informative data	Selection of compounds which provide the greatest amount of information	[73-75]
Correlative	Identification of relationships between variables based on a correlation matrix	Testing the hypothesis concerning the independence of the parameters in the model	[78, 119]
Factorial	"Reduction" of information by introducing new variables representing linear combinations of the original data	Determination of the "structure" of the data, the extent to which the items and parameters in the model may be grouped	[79-82]
Regression and dispersion	Construction of a functional relationship between independent variables and the response (dependent variable)	Determination of the quantitative relationship between structural parameters and the bioactivity expressed by the compounds	[31, 61-68] [85-87]

For example in communication[70] attention is drawn to the irrational use of the Hansch model proposal concerning the normal rule for the distribution of the variables included in this model. Analysis of fourteen possible distribution rules for the variables in the Hansch model showed that, regardless of the hydrophobicity characteristics of the biologically-active compound, the best model for describing the transport of a compound to the bio-target is the exponent of a power rule for the size distribution of the hydrophobicity parameter with a clearly pronounced assymetry. The structure of this distribution indicates that the probability of the substrate reaching the site of action increases in proportion to its hydrophobicity in accordance with the power rule and decreases in accordance with the exponential rule. The presence of asymmetry indicates that random events in a given system are not always mutually-independent. The presence of a correlation between "independent" parameters is one of the most widespread reasons for the low predictive capacity of the derived relationships. The emergence of models, which do not effectively predict quantitative structure-activity relationships, in addition to "technical" features of the regression analysis, is associated with a number of fundamental difficulties: a) in establishing the uniformity of the mode of interaction between the group of compounds under investigation and the same receptors;[1] b) in selecting a regression model conforming to the mode of action of the compound; c) in selecting variables which adequately describe the property under analysis; d) in the use of bioactivity data obtained by different research workers (the problem of accuracy and reproducibility of a biological experiment); e) in establishing the relationship of the resultant biological activity of a compound, which affects many physiological processes occurring in the body.

On account of the above-mentioned difficulties and because there is currently no alternative to a regression analysis for obtaining a quantitative prediction of the magntitude of bioactivity, an alternative proposition would be to construct regression models after a preliminary qualitative analysis of the available data had been carried out. In this case an analysis of a quantitative structure-activity relationship could have the following sequence. In the first stage of the preliminary or, as otherwise termed, the "exploratory"§ analysis, the general structure of the data is established. For this purpose one may use graphic display of the multidimensional space of the data, and also automated methods of classification and statistical treatment of the information. At this stage within the limits of the structure-activity determination two problems may be resolved, i.e. to separate classes of related compounds, and to convert to a set of a significantly smaller number of informative parameters describing the structure of the compounds. In the following stage the hypothesis concerning the independence of parameters in the model may be checked with the aid of correlation analysis methods.[78] If necessary, by using factorial analysis methods, factors which represent a linear combination of the original parameters in the model may be introduced into the regression model.[79-82] It has been recommended[18] that the following rules should be obeyed, when the final regression model is being constructed: 1) at the preliminary analysis stage as many independent parameters as possible should be examined as model variables; 2) to select from the various combinations of variables those which contain parameters related to the different types of interaction (for example $\log P$ and σ [83]); 3) to disregard regression coefficient variables with a low level of significance; 4) to select a model with the lowest standard deviation, when the values of the correlation coefficients are similar; 5) in order to exclude random correlations, at least five–six results of the biological tests for each parameter tested in the model should be included;[84] 6) other conditions being equal to give preference to simpler models; 7) with the objective of reducing and simplifying the calculations and avoiding fundamental errors to take into account the reality of the proposed model from the point of view of the phenomenon under examination.

One should also take into account the potentialities of modern regression analysis in regard to the evaluation of the quality of the regression dependences obtained.[85-87] By correct construction of the regression dependence, a model describing the action of the biologically active compound may be obtained which has high predictive capacity and it is thereby possible to resolve the problem of optimising properties in a series of related compounds. However, it remains an open question whether it is possible to predict bioactivity of compounds which differ in structure. Resolution of this problem is dependent on the identification of common structural elements.

2. Identification of Common Structural Elements in Biologically Active Compounds

The suggestion that the biological activity of a compound results from the presence of certain molecular substructures (pharmacophores) patterns the basis for the search for common structural

§P.F.Velleman and D.C.Hoaglin, "Applications, Basics and Computing of Exploratory Data Analysis", Duxbury Press, Boston, 1981, p.354.

elements in compounds. A typical feature of this approach is the use of pattern recognition techniques (PRT)[87-89] for dividing compounds into active and inactive species according to a set of structural parameters. In these terms the Free-Wilson model,[90] based on the additive contribution of substructures in substituents to the bio-activity value, occupies an intermediate position between quantitative regression models and qualitative models of pattern recognition techniques. With this simple model it is possible to narrow down significantly the area in which searches are made for effective biologically active compounds. For example, when testing compounds in which substituents may occupy four positions or when the number of the substitutions is changed from three to five, use of the Free-Wilson method reduces the number of bio-tests required from 120 to eleven.[18] However, since information is used at the qualitative level concerning the presence or absence of certain types of pharmacophores in the structural formula of compounds, a quantitative prediction of the bio-activity value is often found to be unreliable. Thus attempts have been made to improve this model by linking the latter with the mode of action of compounds[91-94] or by including the mutual effect of the substituents in the examination.[95] However, in the latter case there is a sharp increase in the number of variables in the model and the model becomes difficult to operate.

In the case of items which may be described by a large number of parameters, pattern recognition techniques based on the automatic classification of items according to similarity or lack of similarity are found to be more effective.[96] Methods related to the three types of analysis (Table 2) are most frequently encountered in the literature concerning structure-activity determinations.

Table 2. Main Methods for Identifying Common Structural Elements and Classification of Compounds.

Form of analysis	Method of processing information	Field of use	Refs.
Discriminant	Construction of separating hyperplanes according to an instruction selection consisting of two classes of items	Selection of informative parameters of the model for describing the structure and classification of the compounds into active and inactive	[14, 77, 97-101]
Linear instruction machine	Non-parametric discriminant analysis, based on the correction of an incorrect classification by means of the inverse relationship in the iterational process	Ditto	[14, 88]
Logical-structural	A form of discriminant analysis based on the use of the laws of inductive logic	Ditto	[17]
Cluster	Classification of items according to similarity or differences with the aid of optimisation of the efficiency function	Classification of compounds according to types of activity	[102-107]
Modelling of spatial structure properties of the molecule	Calculation and construction of three-dimensional images of molecules by quantum chemistry and molecular mechanics methods with the aid of molecular graphics	Determination of the steric specificity of substrate-receptor interaction	[110-116, 119]

Discriminant analysis[97-101] is based on the division of compounds into active and inactive species by constructing a separating hyperplane or some other surface in the space of the parameters of the compounds which describe their structure. In the limits of this analysis a selection of the most informative parameters from the point of view of separating the compounds is presented, a separating surface is constructed, and the effectiveness of the resultant discriminant model is tested on instruction and examination selections of compounds. Certain data cited in the literature[99-101] serve as examples of the successful use of discriminant analysis.

Logical structural analysis[17] uses algorithms of discriminant analysis methods in which information is presented in a natural form for the research worker. Many procedures for processing information are directed towards the dialog mode of computer operation.

Cluster analysis[102] involves the grouping of items as concentrations of points in multidimensional space which describe these items of the parameters. This kind of analysis is clearly associated with multidimensional scaling techniques (mapping of the points of multidimensional space on a surface of smaller dimensions) and numerical taxonomy (separation of items into pre-determined classes). The absence of empty clusters is a distinctive feature of cluster analysis techniques. Cluster analysis methods may be used in structure-activity determinations either independently[104-106] or in combination with other methods.[77,107,108]

In all automatic classification methods the studied topological and topographic features of molecular structure are represented in the form of a set of indexed parameters, geometric descriptors which are coordinates of the compounds like points in the multidimensional space of the parameters. In recent years with the development of computer graphics it has become possible to produce a visual three-dimensional image of the molecular structure on the graphic display screen of a computer.[108-110] This has initiated yet another approach in structure-activity relationship studies, the molecular modelling of the spatial structure of compounds.

The most productive approach was found to be the use of methods for modelling the three-dimensional structure of molecules in order to study the spatial specificity of the substrate-receptor interaction by the "lock and key" principle,[110] especially when the electronic pattern of the molecule is represented as surfaces surrounding a nuclear skeleton of the molecular conformation[27] obtained with the aid of a quantum-chemical calculation[111] or the molecular mechanics method.[36] By using this approach it is possible to determine the similarity between the electron-topographical properties of the molecules which is not discernable with the other analytical methods. The quantitative aspect of the calculation of steric specificity of the substrate-receptor interaction has been developed in a regression analysis,[112-115] although a trend towards the combined use of molecular modelling techniques and regression analysis has recently become apparent[115-116] and this should ultimately lead to a system approach to the determination of structure-activity relationships.

3. The System Approach to the Analysis of Structure-Activity Relationships

The concept of the system approach to the analysis of structure-activity relationships involves the creation of a single model for the search for biologically active compounds covering both qualitative and quantitative and also a priori information on the class of compounds studied within the limits of the expert system, which includes a corresponding group of methods for determining structure-activity relationships. The usefulness of this approach is dictated by the need to take into account all information available to the research

worker and also by the selection of the optimal method for processing the information. In fact, if for example the problem of binding between receptor and substrate is defined as a problem of finding the distribution density function of the probability of complex formation according to a set of parameters characterising the structure of the substrate, it becomes apparent that there is a link between this problem and that of the reduction in the dependences under conditions of the inverse incorrect problem.[87] From the theory for the resolution of similar problems[117] one might conclude that the quality of the result obtained is to a marked extent dependent on the degree of detail in which a specific problem is investigated and the selection of the corresponding method for resolving the problem. Since at the various levels and stages of the analysis of structure-activity relationships the research worker presents information differing in quantity, quality and form in which it is presented and usefulness, there obviously is a need to use not one method for determining structure-activity relationships but a range of methods in a sequence which would ultimately lead to a quantitative prediction of the magnitude of the biological activity possessed by an unexamined compound on the basis of parameters characterising the structure of the compound.

The first stage towards combining qualitative and quantitative methods of analysis of structure-activity relationships within a single model was the elaboration of a physicochemical strategy similar to that described in Section III.

The potential of a system analysis of structure-acitivity relationships in this approach was linked with the formation of a unified description of the electron-topographical properties of molecules based on a single donor-acceptor model representing the substrate-receptor interaction, in which the model parameters could be extended as indicator variables at the automatic compound classification stage and as quantitative variables on reduction of the structure-activity regression dependences. This poses the problem of optimising the properties in the series of compounds with different structural formulae including those which belong to different classes but which have similar donor-acceptor and topographic properties of the descriptor centres.

The present tendency to integrate the methods and approaches in the structure-activity relationship determination is also reflected in the packages of programmes currently being elaborated.

V. SOFTWARE PACKAGES FOR DETERMINING STRUCTURE-ACTIVITY RELATIONSHIPS

In order to perform the methods and approaches considered for the analysis of structure-activity relationships, relevant software packages must be produced. Currently-available software packages differ both in function and in the extent to which they cover the problem to be resolved, and also in the class of computer in which they may be used. Software packages designed according to the modular principle with a dialog operation regime are most convenient. Such packages are usually designed for use in mini-computers, and on account of the ease with which new programmes can be incorporated into the package, they undoubtedly have an advantage over other software packages in regard to the production of an expert system for determining structure-activity relationships based on a laboratory mini-computer.

By way of an example four of these packages will be examined in which previously-described approaches to the analysis of structure activity relationships are performed: automatic classification based on methods for recognition of samples (ADEPT), logical-structural method (TOPLOG), molecular modelling (MOLY), and physicochemical (RASTR) approaches.

The ADAPT software packages[14] based on processed information contains the structural formulae of the compounds. Any of them may be entered into the computer by building its image on a graphic display monitor with the aid of a special set of commands in the interactive mode. The structural formulae entered are stored in the form of a connection matrix on discs (disc drives). It is envisaged that there could be facilities for the addition, exclusion, alteration, and recalling of the stored structures of compounds. Structure-activity relationship analysis is based on the methods of parametric and non-parameteric statistics and recognition of the items: linear regression, discriminant analysis; a linear instruction machine, and classification according to the number of close neighbours. The ADEPT system operates on the basis of a 16-bit MODCOMP II/25 minicomputer and together with the data bank occupies approximately 2 Megabites of memory on magnetic discs.

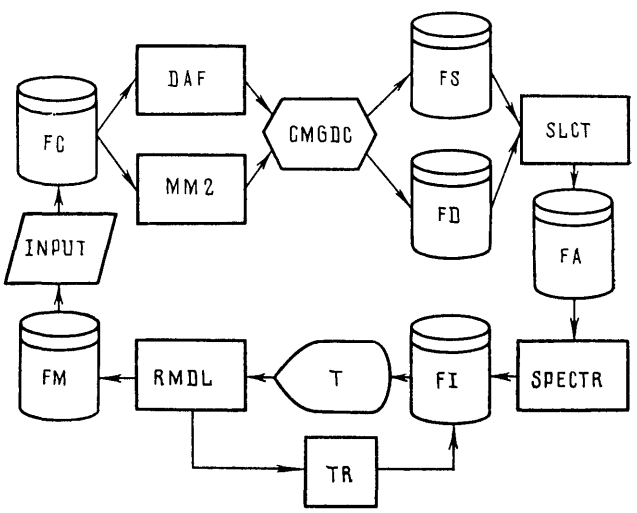
The software package TOPLOG[17] offers the user a more advanced system of input, editing, and information conversion to a form which is acceptable to the research worker. This is reflected in the file system of the package which counts 14 types of files with different functions. The package includes a procedure for achieving a logical-structural approach like that described in reference 17. A distinctive feature of the TOPLOG package is the inclusion of an algorithm for selecting common structural fragments of molecules based on an analysis of graphic representations of structural formulae of the compounds under investigation. The package consists of 14 programmes with a total capacity of approximately 8000 fortran operators and it may be run in an HP-1000 minicomputer.

In contrast to the packages described in which the main type of information is the structural formula of compounds, in the MOLY package[10,118] in order to construct a biologically-active compound a stereoscopic three-dimensional image of the molecule is used in which its properties are represented (for example surfaces of electrostatic potential). With the aid of molecular modelling techniques it is possible to obtain parameters of the molecule structure which reflect the spatial specificity of the interaction between substrates and receptors and which may be used for constructing regression models of quantitative structure-activity relationships. The MOLY package contains approximately 15 000 fortran operators and occupies 1 Megabite of memory.

In the RASTR (recognition of active structures)¶ software packages procedures are included which provide a physicochemical approach for the detection of common fragments of biologically active compounds according to the electron-topographic properties in structure-activity determinations. A feature of this package is that a system approach to the analysis of structure-activity relationships may be achieved by using a set of previously-examined methods at different stages of the study (Tables 1 and 2). This is achieved by means of a unified description of the electron-topographic properties of the molecules from the position of a single donor-acceptor model of the substrate-receptor interaction. For example one possible operational variant with the RASTR package may be as follows. The structural formula of a compound and

¶O.A.Raevskii and A.M.Sapegin, Khim.-farmatsevt. zhurn., 1987, **21**, 1338; A.M.Sapegin, A.N.Razdol'skii, V.V.Chistyakov, and O.A.Raevskii, Khim.-farmatsevt. zhurn., 1987, **21**, 1341.

information on the type of atoms contained in the formula are introduced from the computer terminal. With the aid of an INPUT programme (Fig.1) these data are converted into a connection matrix and are entered into the compound file on a magnetic disc. Information from this file is used for calculating a descriptor centre geometry matrix, a physicochemical "portrait" of the molecule describing donor-acceptor and topo-graphic properties of the active centres in the substrates. Diagonal elements of the descriptor centre geometry matrix are coded on the basis of calculated values of donor-acceptor factors in the descriptor centres in accordance with a unified scale of a donor-acceptor interactions. An algorithm for calculating the donor-acceptor factor of the descriptor centre (DAF programme) is constructed in order to analyse the tree of a graphic representation of the compound's structural formula using a data bank of Taft constants for different types of atoms and correlation equations for calculating the Taft constant of complex substituents and the donor-acceptor factor of the descriptor centre.[50,52-53] Extra-diagonal elements of the descriptor centre geometry matrix contain information on the topography of the descriptor centres in the form of the distance between respective descriptor centres for equilibrium conformations calculated by the molecular mechanics method[36] (programme MM2). The descriptor centre geomtry matrix is formed by the CMGDC programme which operates in two modes: analysis of structure-activity relationships, and in a mode for logging the descriptor centre geometry matrix into the data bank.



Operating configuration for the main nucleus of the RASTR package Programmes: INPUT, Input; DAF, calculation of donor-acceptor factors; MM2, calculation of equilibrium conformations of molecules by the molecular mechanics method; CMGDC, formation of descriptor centre geometry matrix; SLCT, selection of common structural fragments; SPECTR, construction of the spectrum of interatomic distances; RMDL, construction of regression models; TR, transformation of regression models of the pharmacophores into the spectrum of interatomic distances; files: FC, compounds; FS, structures; FD, structures in data bank; FA, activities (of pharmacophores); FI, images (spectra of interatomic distances); FM, regression models.

With the aid of the SLCT programme common structural fragments are selected for the compound under investigation (FC file) and compounds stored in the data bank (FD file). The procedure for searching for common structural fragments is analogous to that used in the TOPLOG package.[24] It differs only in that in this instance the common structural fragment is considered to be not a strict identity of the elements in the structural formula of the compound but their closeness with respect to electron-topographic properties which may be regulated by the research worker. The isolated fragments are potential pharmacophores and are entered into the biologically active structure file (FA file).

The descriptor centre geometry matrix of common structural fragments in the biologically active compounds which are contained in the FA file may be represented (with the aid of a SPECTR programme) as a range of interatomic distances, which is convenient for a visual comparison of the structures of the compounds or as a set of structural parameters for constructing regression models of structure-activity relationships. Interatomic distance spectra are stored in the "Images" file (FI file).

Thus at the stage described above the problem of identification of potential pharmacophores is qualitatively resolved, i.e. on the basis of indicator parameters of the donor-acceptor model a concept can be formed concerning the electronic and spatial properties of the active centres in substrates responsible for a particular kind of biological activity.

The next important step is to determine the quantitative relationship between structural parameters of the compound and the magnitude of the biological response. In the RASTR package examined the original information for the construction of regression models (RMDL programme) is the information from the FI file. The search for the optimal regression dependence is based on the principle of the structural minimisation of mean empirical risk.[87] The predictive capacity of the model is assessed according to a test selection of data.

Results obtained at the regression analysis stage may be repeatedly used in the RASTR package for designing a more accurate model or for constructing a new model. These data are stored in the FM file. As a result of the file organisation for transfer of information between programmes in the package, the system is highly flexible as regards the inclusion of standard or original methods for processing information at any stage in the study, and may accept all kinds of quantitative structure-activity relationship analysis, the main condition for constructing an advanced expert system.

All programmes in the package have been written in FORTRAN-77 language and are used in a NORD-10 minicomputer (OZU capacity, 128 kilobites).

The programme packages examined indicate that nowadays the software covers a wide range of algorithms for processing structural information and thereby creates the basis for a system approach to the analysis of structure-activity relationships. This objective could be achieved in practice by elaborating a problem-orientated expert system for the construction of compounds with desired properties.

VI. CONCLUSION

In order to search for effective biologically active synthetic compounds in accordance with the basic principles of constructing compounds with desired properties, the following problems must be resolved: 1) identification of the compound interacting with the

receptor; 2) determination of the electron and spatial structure of the compound; 3) the correct description of the structure within the limits of the computer used; 4) derivation of statistically significant data on the biological activity of the compounds; 5) optimisation of a method or group of methods for resolving specific problems related to the determination of structure-activity relationships.

Table 3. Examples of correct predictions of structure-activity relationships.[119]

Type of compound	Form of bioactivity
Benzothiadiazines	Hypotensive action
Propinylamines	Monoamine oxidase inhibition
N-(Phenoxyethyl)-cyclopropyl-amines	Monoamine oxidase inhibition
β-Carbolines	Monoamine oxidase inhibition
Sulphonamides	Carboanhydrase inhibition
Carbanoylpiperidines	Choline esterase inhibition
Ketones	Chymotrypsin inhibition
Benzylpyridinium ions	Inhibition of complement
Steroids	Binding with progesterone receptor
Esters	Papain hydrolysis
Dopamine esters	Hydrolysis of arylamidases
Peptidyl-*p*-nitroanilines	Subtilisin hydrolysis
Polycyclic aromatic hydrocarbons	Hydroxylation of microsomal oxidase
Isatin-β-isothiosemicarbazones	Antiviral carcinogenicity
Pyrazoles	Ditto
Cytidine derivatives	Cytostatic, immunodepressive
Nitrosourethanes	Cytostatic
Mitomycins	Ditto
Hydantoin derivatives	Ditto
Rifamycin amides	Antibacterial
Sulphonamides	Ditto
Erythromycins	Ditto
Quinoxaline-1,4-dioxides	Ditto
Phenanthrenes	Antimycoplasma activity
Phenylamidinourethanes	Ditto
Naphthoquinones	Ditto
Tuberines	Ditto
Methoxychlorines	Insecticidal
N-Hydroxypyridones	Fungicidal
Pyridine derivatives	Ditto
Trifluoromethane sulphonamides	Herbicidal
Alkylarylcarboxylic compounds	Ditto
Aromatic esters	Ditto
Piperidinoacetanilides	Phytoactivity
Pyrimidones	Inhibition of the Hill reaction
Urethanes	Herbicidal
Phenylacetamides	Hypnotic
Pyridylmethanes	Spasmolytic
Pronazines	Neuroleptic
Aromatic and aliphatic acids	Anti-inflammatory
Benzothiopine derivatives	Neuroleptic
Carboxylated esters	Antithrombic
Acrylates	Toxicity
Copper chelates	Cytotoxicity
Pyramine amines	Immunodepressive
Azapurine-6-ones	Immunodepressive
Phenyloxazolidines	Radioprotectant
Carbonoylethylamines	Cholinolytic
Triazines	Dehydrofolate reductase inhibition
Benzdiazepines	Anti-pentylene tetrazolium activity
Cyanocyclohexylamines	Fungicidal
Piperidinoacetanilides	Anti-serotonin activity
Somatostatin analogues	Antidiabetic
Steroids	Progesterone activity
Azacycloalkanes	Analgetic
Organosilicon amines	Fungicidal
Inda-1,3-diones	Toxicity
Sulphones	Antibacterial
Alkobenzylalkylamines	Toxicity
Spirobarbituric acids	Sedative
Adenosine analogues	Hypotensive
Trimethoprim analogues	Antibacterial

An incorrect approach to the resolution of any of the above-mentioned problems could impede the determination of the "true" structure-activity relationship or even lead to the proposal of a false relationship. For example identification of the substrate with a substance introduced into the body (i.e. disregard of the possibility that chemical and biochemical transformations of the chemical may occur during transportation from the site of administration to the bio-target) sometimes causes complications in the detection of common structural fragments among compounds expressing a particular kind of biological activity. Approximation of a model describing the electronic and spatial structure of compounds automatically affects the predictive potential of the model. The efficiency of the latter may also be determined by selecting a method for processing the information, i.e. its compatibility with the form of the presentation and level of information on the structure and properties of the molecules.

There are now many examples in the literature concerning the correct prediction of the biological activity of compounds (Table 3).[19] However, most of these studies are concerned with the optimisation of properties within a series of related compounds. A qualitatively new level in quantitative structure-activity relationship determinations, which would lead to the identification of essentially new classes of effective compounds, would only be attainable by using methods for the selection of common structural fragments within a diverse range of compounds with subsequent optimisation of the useful properties which they express.

This leads to the need to develop a system approach to the determination of structure-activity relationships which should include, in addition to the previously-considered questions, an extended section of chemical data[120] and artificial intelligence.[121] The ultimate stage in a system investigation of a structure-activity relationship could include a plan for synthesis and technological schemes for producing the new compounds.[122,123] Development of this strategy should eventually transform an empirical approach for structure-activity relationship determinations into a fundamental scientific approach exploiting the advances in chemistry, physics, biology, and information technology. A powerful platform will thereby be created for the cost-effective construction of compounds with desired properties for the needs of industry, agriculture, and medicine.

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While this review was being prepared for publication a significant number of papers appeared in the literature on studies dealing with virtually all aspects of the question of targeted screening and the construction of effective biologically-active compounds. Worthy of mention are a paper presented at the Sixth European Symposium on Quantitative Structure-Activity Relationships[124] and a monograph[125] in which the fundamentals of the construction of systems for determining the main kinds of bioactivity for large numbers of compounds are presented.

The approach concerned with the three-dimensional perspective of molecular structure by molecular graphics techniques[126–131] based on empirical[132,133] and quantum-chemical[134,135] calculations of molecular conformations or the corresponding X-ray data[136,137] is progressing in an interesting manner. Considerable attention is being focused on the elaboration of models for describing structure with the aid of sets of descriptors[138–149] and on the visual representation of results obtained from the statistical analysis of structural information.[150–153]

Closer examination of the physicochemical content of quantitative structure-activity relationship models[154–157] including the radical changes in programming technology in expert systems[165–171] together with the pharmacodynamic and pharmacokinetic stage[158–164] should be included in the new trends in structure-activity determinations.

The creation of an expert system for quantitative structure-activity relationships could become essential for the formation of a unique "programme" theory for the targeted search and construction of biologically active compounds.

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Short-range Order and Local Displacements of the Atoms in Non-stoichiometric Compounds

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Published data on the local distribution of the atoms and their displacements in non-stoichiometric transition metal carbides and nitrides have been reviewed. The phenomena of short-range order in disordered and ordered non-stoichiometric compounds, and their solid solutions, have been discussed in detail. Data on the static displacements of the atoms in disordered carbides and nitrides have been analysed. The possibilities for the further study of the distribution of the atoms in non-stoichiometric compounds have been discussed.
The bibliography contains 79 references.

CONTENTS

I. Introduction 913
II. Short-range order in non-stoichiometric compounds 914
III. Short-range order in carbide solid solutions 921
IV. Local displacements of the atoms 922

I. INTRODUCTION

In recent years there has been a continuous increase in interest in the study of the structures of transition metal carbides and nitrides. This is due chiefly to the use of highly sensitive experimental methods, which have established that the distribution of non-metal atoms in these compounds is not statistical, as previously assumed. Another reason for the interest in non-stoichiometric carbides and nitrides is related to their properties. These compounds are among the most refractory materials; the melting points T_f of most of them exceed 3500 K, and tantalum carbide has the highest known melting point, T_f = 4270 K; they are radiation-stable superconductors with transition temperatures to the superconducting state $\leqslant 17$ K. In addition, they are extremely hard, their hardness approaching that of diamond. Another characteristic of non-stoichiometric compounds is the possible formation of unrestricted reciprocal solid solutions, so that their physicochemical characteristics can be influenced considerably by replacing the metal and non-metal atoms. The properties of non-stoichiometric compounds are directly related to their structural state, that is to the presence or absence of correlations and short-range or long-range order in the relative positions of the atoms.

In the present work, an attempt has been made to systematise the comparatively few but nevertheless important data obtained in the last 10–15 years in the study of the local distribution of the atoms and their displacements in non-stoichiometric compounds and their solid solutions. Before discussing these results, however, it is appropriate to give a general description and examination of the principal characteristics of the crystal structure and the chemical bonding in non-stoichiometric compounds of the transition metals, necessary for the subsequent discussion.

Non-stoichiometric compounds are often called interstitial phases, indicating that a characteristic of their structure is the presence of a face-centred cubic (FCC) or hexagonal close-packed (HCP) metal lattice with interstitial non-metal atoms in the octahedral interstices. At the same time, the symmetry of the metal lattice in the carbides and nitrides differs from that of the crystal lattice of the corresponding transition metals, that is the crystal structure of the metal changes on formation of the carbides and nitrides (cobalt is an exception). The group IV transition metals (titanium, zirconium, hafnium), which have an HCP structure, form carbides and nitrides with an FCC metal sub-lattice. Transition metals with a body-centred structure (vanadium, niobium, tantalum, chromium, molybdenum, tungsten) form carbides and nitrides with FCC or HCP metal sub-lattices. The change in the crystal structure of the metal on formation of the carbide or nitride indicates fairly strong interactions between the metal and non-metal atoms, so that the application of the term "interstitial phase" to these substances is not completely justified. In the narrow sense of the word, only restricted interstitial solid solutions are true interstitial phases.

The concept of "interstitial phase" (or "interstitial alloy") has recently been used fairly widely. It is used to describe a wide range of phases with related structures, formed as a result of the insertion of hydrogen, nitrogen, carbon, oxygen, boron, or silicon atoms into the interstices in the crystal lattice of a transition metal. Both interstitial solid solutions and the transition metal hydrides, carbides, nitrides, oxides, and borides, and also the reciprocal substitutional solid solutions formed by these compounds, are interstitial phases. These compounds are also called compounds of variable composition, emphasising the existence of wide homogeneity ranges, within which the composition of the compound may deviate considerably from the stoichiometric composition with preservation of the crystal structure. Since the deviation from stoichiometry, that is non-stoichiometry, is a characteristic property of these compounds, it is more correct to call them non-stoichiometric compounds of the interstitial phase type. This term emphasises that these substances (carbides, nitrides, etc.) are compounds, and not interstitial solid solutions, and at the same time draws attention to the most important characteristics of their structure, namely the location of the non-metal atoms in the interstices of the metal sub-lattice and the possibility that the composition deviates considerably from the stoichiometric.

In the full sense of the term, only the carbides, nitrides, and lower oxides of the transition metals can be described as non-stoichiometric compounds of the interstitial phase type. Thus the stability of the hydrides and the limiting concentration of hydrogen in them may change with change in the external conditions. The difference between transition metal hydrides and solid solutions of hydrogen in transition metals therefore becomes indistinct. The borides and

more particularly the silicides have practically no homogeneity ranges; moreover, in these materials a fairly important role is played by direct B—B and Si—Si bonds (in the carbides, nitrides, and oxides, direct interactions between the non-metal atoms are negligible). The higher oxides also have practically no homogeneity ranges. In the present review, therefore, the carbides, nitrides, and lower oxides of the transition metals are regarded as non-stoichiometric compounds of the interstitial phase type.

A characteristic feature of non-stoichiometric compounds is the, as it were, independent existence of the sub-lattice of the pure metal, which acts as the matrix for the atoms which are introduced into its interstices and which form the non-metal sub-lattice. The pure metals can be regarded as a unique type of interstitial phase corresponding to unoccupied interstices, and the unoccupied interstices can be regarded as "holes", equivalent to interstitial atoms. When the non-metal sub-lattice is partly occupied, the unoccupied interstices (structural vacancies) can diffuse through the lattice and behave like real interstitial atoms. Thus the structural vacancies in non-stoichiometric compounds of the interstitial phase type can be regarded in a first approximation as analogues of interstitial atoms.[1-4] Thus deviation from stoichiometry can be (and is) examined using the theory of substitutional solutions, whose components are interstitial atoms and structural vacancies. The deviation from stoichiometry leads to a change in all the properties of non-stoichiometric compounds.[3-9] The defect character of the crystal structure, that is the presence of a high concentration of structural vacancies, is apparently one of the most important characteristics of non-stoichiometric compounds.

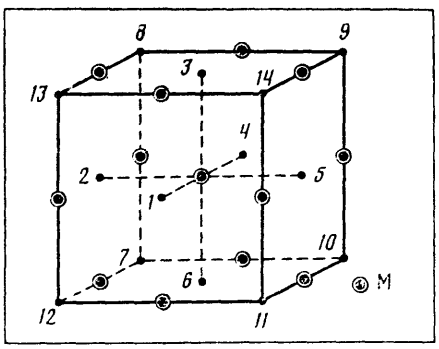


Figure 1. NaCl structure and the immediate environment of the metal atom: (1—6) first coordination sphere, formed by six sites of the non-metal sub-lattice; (7—14) second coordination sphere, formed by eight sites of the non-metal sub-lattice; twelve metal atoms form an independent coordination sphere (M represents a metal atom; the sites of the non-metal sub-lattice are numbered).

Non-stoichiometric transition metal monocarbides, mononitrides, and monoxides MX have the NaCl structure. In this structure (Fig.1), the non-metal atoms occupy statistically the octahedral interstices of the metal sub-lattice, so that each metal atom is in an octahedral environment of six sites of the non-metal sub-lattice, which form the first non-metal coordination sphere; the second non-metal coordination sphere is formed by eight sites of the non-metal sub-lattice; twelve metal atoms form an independent metal coordination sphere, situated between the first and second non-metal coordination spheres. The lower carbides and nitrides with the composition M_2X have the hexagonal $W_2C(L'3)$ structure, in which the non-metal atoms occupy statistically half of the octahedral interstices.

An analysis of theoretical considerations[10-15] and a large number of calculations by zone and cluster methods led to the formulation[8,16] of the principal regular features of the structure of the valence zone of non-stoichiometric compounds with the NaCl structure. According to Refs.8 and 16, the valence zone of these compounds includes a low-energy $2s$(X) band containing small contributions from the *s*-, *p*-, and *d*-states of the metal; the principal valence-bonding band, formed by strong mixing of the $2p$(X) and d(M) functions; and a high-energy partly occupied conductivity band, formed chiefly by nd(M) functions with a small contribution from $2p$(X), $(n+1)p$(M), and $(n+1)s$(M) functions. The redistribution of the individual atomic states on the formation of non-stoichiometric compounds leads to partial charge transfer between the metal and non-metal atoms, and this is responsible for the ionic component of the chemical bond.

Thus in non-stoichiometric compounds there is a combined covalent—metallic—ionic chemical bond.[8,16] With increase in the concentration of vacancies, the populations of the single bonds M—X increase, but the number of such bonds decreases with a simultaneous decrease in the charge localised on the atoms; this leads to a decrease in the ionic component of the bond. In addition, the deviation from stoichiometry is accompanied by an increase in the width and population of the *d*-band of the metal and a decrease in the width of the $2p$(X) band, and this can be regarded as an increase in the strength of the M—M interactions and a decrease in the covalent component of the M—X bond.

More detailed information on non-stoichiometric compounds can be found in a number of monographs.[1,3-8]

II. SHORT-RANGE ORDER IN NON-STOICHIOMETRIC COMPOUNDS

The presence of structural vacancies and the possibility of their redistribution within the lattice, together with the combined type of chemical bond, are responsible for the fairly wide occurrence in non-stoichiometric compounds of correlations and of short-range or long-range order in the relative arrangement of the atoms.

Any disorder destroys the crystal symmetry and leads to a decrease in the degree of long-range order. The simplest type of disorder occurs in ideal binary substitutional solid solutions. In an ideal solid solution, when an atom A is replaced by an atom B, the crystal lattice is not distorted, and the sites in which this replacement has taken place are distributed randomly, that is statistically, in space. In this case the probability of finding an atom of a given element in any site of the crystal lattice is equal to the atomic fraction of this element in the solid solution. Thus in an ideal solution, the occupancy of a given site by an atom of a given element is independent of the nature of the occupancy of the other sites, both neighbouring and distant. In a real crystal, the atoms of different elements have different masses and dimensions, so that the energies of interaction between atoms of the same kind and atoms of different kinds differ considerably. It is for this reason that statistical

disorder in a crystalline solid can arise only at sufficiently high temperatures, when the forces of interatomic interaction are small compared with the energy of the thermal vibrations. This state can be "frozen" by quenching, that is by cooling rapidly to low temperatures, at which the diffusion mobility of the atoms is negligible.

In non-stoichiometric compounds, statistical distribution of the interstitial atoms and structural vacancies is also obtained by rapid cooling. For a long time it was assumed that for non-stoichiometric compounds this disordered state was the only one possible, and it is only in recent decades that it has become clear that this is not the case. It has been found that on comparatively slow cooling of non-stoichiometric compounds, the statistical distribution gives way to correlations in the arrangement of the atoms and vacancies in neighbouring lattice sites, as a result of which the atoms of a given element may be surrounded preferentially by atoms of the same or another element (or vacancies), that is short-range order may be observed.

The arrangement of the atoms in the crystal lattice of non-stoichiometric compounds can be characterised by the long-range and short-range order. In the present review, particular attention is paid to recent studies of short-range order and the associated local displacements of the atoms in refractory non-stoichiometric compounds and their solid solutions.

The principal experimental methods for studying short-range order in non-stoichiometric compounds of the interstitial phase type are nuclear magnetic resonance (NMR) and the diffuse scattering of neutrons (to study the distribution of interstitial atoms) and X-rays (to study the distribution of metal atoms). None of these methods is universal (applicable to all non-stoichiometric compounds) in giving information on the nature of the distribution of the atoms of all elements. NMR has the most restricted range of applicability, since magnetic resonance signals are given only by nuclei with a non-zero spin I, which have a magnetic moment. Thus NMR studies are possible in principle for non-stoichiometric compounds of vanadium, niobium, and tantalum, since the most abundant isotopes of these metals have nuclei with $I \neq 0$. On the other hand, NMR cannot be used to study the non-stoichiometric compounds of the group IV transition metals (titanium, zirconium, hafnium), since the nuclei of the most abundant isotopes of these metals do not have a magnetic moment.

As far as the interstitial atoms (carbon, nitrogen, oxygen) are concerned, the nuclei of the abundant isotopes ^{12}C and ^{16}O have zero spin, and magnetic resonance cannot be observed. The most abundant nitrogen isotope ^{14}N has a magnetic moment ($I = 1$), but no ^{14}N NMR studies of non-stoichiometric compounds of the interstitial phase type have yet been carried out. The NMR study of the nuclei of the carbon isotope ^{13}C with spin 1/2, which would increase considerably the amount of information on the nature and structure of non-stoichiometric carbides, appears extremely promising.

In those cases where it is possible in principle, the use of NMR to study non-stoichiometric compounds is extremely effective, because of the high sensitivity of the method to slight changes in the symmetry of the environment of the resonating atoms.

1. NMR Studies of Short-range Order

NMR can be used to determine the relative positions of interstitial atoms and structural vacancies in the non-metal sub-lattice of non-stoichiometric compounds, that is to study the nature of the short-range order in them. In addition, NMR reveals various characteristics of the electronic structure of non-stoichiometric compounds.

A special notation will be used for convenience in the subsequent discussion. The immediate environment of a metal atom in a carbide MC_y or a nitride MN_y with the NaCl($B1$) structure includes two coordination spheres formed by sites of the non-metal sublattice, and one coordination sphere formed by metal atoms (see Fig.1). It is convenient to denote the position of a metal atom in this environment by means of subscripts and superscripts giving the numbers of vacancies in the first and second coordination spheres respectively, formed by the sites of the non-metal sub-lattice; for example, the metal atom position M_0^2 indicates that its first coordination sphere is complete (contains no vacancies), while the second coordination sphere contains two vacancies.

Among the non-stoichiometric compounds, the vanadium compounds have been studied in most detail. VC_y specimens with $y = 0.66$, 0.7, 0.8, 0.84, and up to $y = 0.87$, that is throughout the homogeneity range of vanadium carbide, have been studied.[17] The ^{51}V NMR spectra of the carbides $VC_{0.875}$, $VC_{0.84}$, and $VC_{0.70}$ showed several resonance lines, whose intensity changed with change in the composition of VC_y. Comparison of the total intensity of the resonance lines in metallic vanadium and its carbides showed that NMR makes it possible to detect practically all the vanadium nuclei in VC_y, irrespective of its composition. At the same time, the presence of vacancies in the carbon sub-lattice of VC_y had a significant influence on the relative intensity of the observed resonance lines. The lines and their satellites in the ^{51}V NMR spectra were associated with the positions of vanadium atoms in VC_y having definite configurations of the vacancies in the first coordination sphere.[17] This identification was possible since the electric field gradient of vanadium nuclei with no vacancies in the first coordination sphere should be much smaller than that for vanadium nuclei having one or several vacancies. Thus the observed lines were associated with the positions of vanadium atoms V_0 (without vacancies in the first coordination sphere), V_1, V_2, and V_3 (with one, two, and three vacancies respectively in the first coordination sphere).

A relationship was also established[17] between the number of vacancies n in the immediate environment of a vanadium atom and the sharp change in the Knight shift (K):

$$K_n - K_{n-1} \approx nK_0, \qquad (1)$$

where $K_0 \simeq 0.07-0.09\%$, that is the change in K is proportional to the number of vacancies in the first coordination sphere of a vanadium atom in VC_y.

In Ref.17, to investigate the nature of the distribution of the vacancies in vanadium carbide, the experimentally determined probability distribution $P(n)$ of the positions of the vanadium atoms n was compared with the random probability distribution, calculated from the equation:

$$P(n) = C_6^n (1-y)^n y^{6-n}. \qquad (2)$$

The experimental distribution differed from the random distribution for all VC_y specimens studied; for example, the probability of the position V_0 decreases much more rapidly than for the random distribution, and the V_3 positions are encountered much less frequently than in the statistical distribution. The small number of V_3

positions and the absence of vanadium atom positions with more than three vacancies in the first coordination sphere were attributed to repulsion between neighbouring vacancies. Thus the existence of short-range order in a non-stoichiometric compound, namely vanadium carbide, was established experimentally for the first time.[17]

In the same work,[17] NMR was used for the first time to study the ordered phase of a non-stoichiometric compound. The ^{51}V NMR spectrum of $VC_{0.875}$ differed considerably from the spectra of vanadium carbide specimens with other compositions. In particular, the ratio of the intensities of the lines corresponding to the positions V_0 and V_1 was 1/3. If the relative intensity of each line is proportional to the relative number of corresponding positions, this intensity ratio can be explained if in the carbide $VC_{0.875}$ three quarters of all the vanadium atoms have one vacancy in the first coordination sphere, and the others have a complete environment. This distribution of the vacancies indicates the existence of a superstructure of the V_8C_7 type with space group $P4_332$ or $P4_132$. It should be noted, however, that in the opinion of the authors cited,[17] this model of the distribution of the vacancies does not provide a completely accurate description of the real lattice. Thus this superstructure with helical arrangement of the vacancies contains only the positions V_0^1 and V_1^1, whereas study of the satellites indicates the existence of three types of position V_1, which could not be distinguished by the authors cited.[17] Moreover, the proposed distribution of the atoms in the ordered carbide V_8C_7 cannot be described by the space group $P4_332$.

Interesting results revealing another ordered structure were obtained in an NMR study of an annealed single crystal of vanadium carbide $VC_{0.84}$.[18,19] The ^{51}V NMR spectra obtained were broken down into lines corresponding to the positions V_0 and V_1. An analysis of the satellites made it possible to break down the intense line V_1 into lines corresponding to the positions V_1^0, V_1^1, and V_1^2 (without vacancies and with one and two vacancies in the second coordination sphere). The ratio of the intensities of the V_1^1 and V_1^2 lines in the spectra was 2:1, so that in the carbide studied, the number of V_1^1 positions is apparently twice the number of V_1^2 positions. The higher intensity of the lines corresponding to the V_1^1 and V_1^2 positions makes it possible to regard them as the positions of the ordered structure of vanadium carbide. In an electron diffraction study of $VC_{0.84}$,[18] the trigonal symmetry of the ordered vanadium carbide V_6C_5 was proposed; the use of the NMR data on the ratio of the numbers of the positions V_1^1 and V_1^2 made it possible to describe the distribution of the carbon atoms and the vacancies in the trigonal unit cell, that is to determine the structure of V_6C_5. The presence of weak lines corresponding to the positions V_0 and V_1^0 was attributed to the deviation of the composition of the carbide studied from the composition of the ordered phase $VC_{0.83}$ (that is V_6C_5). The presence of these lines in the spectrum may also be related to the deviation of the degree of long-range order in the specimens studied from the maximum possible.

These NMR studies [17–19] gave a qualitative picture of the distribution of the carbon atoms and vacancies in the non-metal sub-lattice of vanadium carbide. The next step was an attempt to obtain quantitative information on the short-range order in VC_y by minimising the ^{51}V NMR spectra.[20,21] The experimental ^{51}V NMR spectra obtained[20] for $VC_{0.75}$, $VC_{0.84}$, $VC_{0.85}$, $VC_{0.86}$, and $VC_{0.87}$ are analogous to the spectra previously described[17] and contain resonance lines corresponding to the positions V_0, V_1, and V_2. Assuming that the complex form of the line in the spectrum is due to the presence in the crystal of nuclei with different local environments, and that the intensity of a signal is proportional to the number of positions of a given type, the following relationship was obtained for calculating the intensity

$$I_p(\nu) = \sum_i \lambda_i P_i I_i(\nu), \qquad (3)$$

where P_i is the probability of the cluster with the i-th configuration of the immediate environment of non-metal atoms round the resonating nucleus (for non-stoichiometric compounds with the NaCl structure, an octahedron of six sites of the non-metal sub-lattice with a metal atom at its centre is taken as the basis cluster figure); λ_i the multiplicity of the i-th configuration of the octahedral cluster; and $I_i(\nu)$ a mathematical model of the ideal spectral line, corresponding to the i-th configuration of the immediate environment of the resonating nucleus (in Ref.20 the lines were described by a Gaussian distribution). The probabilities P_i were expressed by expansion with respect to paired and many-particle correlation parameters by the published method.[22]

The minimisation of the ^{51}V NMR spectra for VC_y with successive allowance for the correlation parameters, beginning with the paired parameters and ending with the sixth-order correlation parameters, showed[20,21] that the best description of the spectrum is achieved by taking account of paired and three-fold correlations. Allowance for correlations of higher orders did not lead to any significant change in the calculated spectrum. According to the results obtained, the paired correlations ε_{21} describing the nature of the distribution of the carbon atoms (or vacancies) in two neighbouring sites of the octahedron situated relative to one another in the first coordination sphere are negative throughout the homogeneity range of vanadium carbide. This means that throughout the homogeneity range of VC_y, the probability of detecting neighbouring vacancies is smaller than that for the statistical distribution. The short-range parameter for the first coordination sphere $a_1 = \varepsilon_{21}/y(1-y)$ is approximately –0.1, increases slowly with the increase in the deviation from stoichiometry, and shows a slight minimum close to the composition $VC_{0.83}$.

Thus the results of the calculation of the correlations and the short-range order parameter in vanadium carbide on the whole agree with the conclusions[17–19] that in VC_y there is short-range order due to the repulsion of vacancies. At the same time, it was incorrectly stated in Ref.21 that the production of the ordered phases of vanadium carbide is due to the existence of a definite type of short-range order. As shown in Refs.23–27, in non-stoichiometric compounds with the NaCl structure, long-range order may not be produced even when there is maximum short-range order in the first and second coordination spheres, so that the existence of short-range order in these compounds is only a necessary but not a sufficient condition for the production of long-range order.

The influence of composition on the ^{51}V NMR spectra of the compounds VN_y ($0.980 \leqslant y \leqslant 0.706$) has been studied.[28] The total intensity of the NMR signal, normalised for the quantity of vanadium, was found to be constant for all values of y. This means that, as in the case of VC_y, in the nitrides VN_y studied all the vanadium nuclei contribute to the resonance absorption line, so that quantitative analysis of the results is possible. The resonance peak observed in the spectra was broken down into two lines, corresponding to the complete position V_0 and the positions of vanadium atoms with one or more vacancies in the first coordination sphere. At a high concentration of vacancies, a systematic deviation of the experimentally observed intensity of the resonance lines from the intensity calculated in the approximation of a random distribution of the nitrogen atoms and vacancies was observed. This indicates that

the nitrogen atoms and vacancies are distributed with a certain degree of order in the non-metal sub-lattice of vanadium nitride.

A quantitative analysis of the short-range order in vanadium nitride was carried out[21] using the same scheme as for vanadium carbide. Minimisation of the NMR spectra established a regular change in the paired and three-fold correlation parameters with change in the composition of the nitride VN_y. According to the calculation, throughout the homogeneity range of VN_y, the parameter ε_{21} is negative and decreases, and the parameter ε_{22} is positive and increases, with increase in the number of vacancies. This means that in vanadium nitride there is short-range order with preferential arrangement of the vacancies at opposite vertices of the octahedron, whose six sites form the first coordination sphere of the vanadium atom.

Cubic vanadium monoxide VO_y has been studied by spin echo and broad-line NMR methods in the temperature range 1.4 to 300 K.[29,30] The ^{51}V NMR spectra showed only one line, whose width increased with increase in the oxygen concentration in VO_y. The measurements also showed that the magnitude of the Knight shift is independent of temperature and the composition of VO_y.

NMR has been used to study short-range order not only in non-stoichiometric compounds of vanadium, but also in solid solutions, chiefly vanadium oxide carbides and oxide nitrides.[21,31] The ^{51}V NMR spectra of the oxide carbides VC_xO_y consist of sets of four lines, whose widths and positions are practically independent of the composition of the oxide carbide. From a comparison of the integral intensity of the ^{51}V NMR spectra of the carbide $VC_{0.87}$ and the oxide carbide VC_xO_y ($x + y = 0.75-0.94$), it was concluded[21] that all the vanadium nuclei contribute to the spectrum of the oxide carbide; in the oxide carbides rich in oxygen ($y \geqslant 0.4$), vacancies are present not only in the non-metal sub-lattice but also in the metal sub-lattice, but no influence of the vacancies in the metal sub-lattice on the integral intensity of the NMR spectra could be detected.

In the analysis of the NMR spectra, the observed lines were associated with non-equivalent positions of the vanadium atoms; it was noted that the intensity of the lines is determined by the concentration of oxygen in the specimens studied. According to Ref.21, all the lines correspond to a complete environment of C and O atoms simultaneously round the vanadium atoms, but the ratio of the numbers of C and O atoms may be different, for example $[VC_5O_1]$, $[VC_4O_2]$, $[VC_1O_5]$, $[VC_3O_3]$. The intensities of the lines in the spectrum are determined by the probabilities of the corresponding positions. Comparison of the experimentally determined values of the probabilities with the values calculated assuming a statistical distribution of the C and O atoms showed that the distribution of the non-metal atoms is close to random for $V_{0.61}O_{0.14}$ and $VC_{0.67}O_{0.15}$, and differs considerably from the random distrubtion at high oxygen concentrations.

In the ^{51}V NMR spectra of the oxide nitrides VN_xO_y, the authors cited[21] observed three lines, two of which, by analogy with VC_xO_y, were associated with the positions $[VN_5O_1]$ and $[VN_3O_3]$.

An analysis of the ^{51}V NMR spectra of solid solutions VC_xO_y, VN_xO_y, and VC_xN_y [21] established that the replacement of one of the atoms forming the immediate environment of a vanadium atom by an atom of another element leads to an increase in the Knight shift compared with that for a uniform complete environment. The highest value of the Knight shift is observed for equal numbers of the atoms of the two elements in the first coordination sphere of the vanadium atom. It may be noted that in vanadium carbide, nitride, and oxide, the Knight shift also increases with increase in the number of vacancies in the immediate environment of the vanadium atom.

Taken together, these data indicate that the introduction of any impurity defect into the immediate environment of the metal atom in a non-stoichiometric compound should lead to an increase in the Knight shift compared with that for a uniform complete environment (the particles whose relative fraction in the first coordination sphere of the metal atom is smaller are regarded as the impurity defect).

Only a few papers have been devoted to the ^{93}Nb NMR study of non-stoichiometric compounds of niobium. Here, mention may be made of Ref.32, where NMR was used for the phase analysis of niobium nitride NbN_7. According to the results obtained, the phases correspond to definite lines in the NMR spectrum, and it is possible to establish from the spectrum which phases are present in the specimen being studied. It was also noted[32] that the quadrupole interactions in niobium nitride are stronger than those in vanadium nitride.

In the ^{93}Nb NMR spectra of NbC_y specimens,[17] only one line was detected, whose intensity decreased rapidly on going from $NbC_{0.94}$ to $NbC_{0.90}$; the intensity of this line decreased only slightly with further decrease in the carbon concentration. This line was assigned to the positions of niobium atoms having a complete environment as far as the third coordination sphere.

The short-range order in NbC_y has been studied in detail by highly sensitive pulse NMR spectroscopy.[23,33-36] Specimens of non-stoichiometric niobium carbide NbC_y ($0.995 \leqslant y \leqslant 0.75$) were obtained by sintering niobium and carbon powders. To obtain niobium carbide specimens in states with different degrees of order, the specimens synthesised were subjected to thermal treatment under different conditions of temperature, heating time, and rate of cooling. The conditions of the thermal treatment had a significant influence on the phase composition of the specimens; heating at temperatures above the temperature of the order–disorder transition (1304 K for $NbC_{0.83}$ [23]) with subsequent quenching (conditions *a*) gave niobium carbide specimens in the disordered state. Heating at 1300 K with subsequent slow cooling (conditions *c*) led to the formation of an ordered phase. Heating at 1300 K with rapid cooling (conditions *b*) gave specimens containing ordered and disordered phases simultaneously. The conditions of thermal treatment will subsequently be indicated after the niobium carbide composition, for example $NbC_{0.88}(c)$.

The ^{93}Nb NMR spectra of the carbides NbC_y, obtained[23,33,34] on a Bruker SXP4-100 pulse spectrometer at frequencies of 22.0, 21.5, and 14.01 MHz, are shown in Figs.2 and 3. Most of the spectra contain a line *O*, whose position coincides with that of the line observed[17] in the NMR spectra of niobium carbide. With increase in the defect character of the carbon sub-lattice, this line becomes less intense and then disappears; in spectrum IV, however, corresponding to $NbC_{0.75}(b)$, the line *O* appears again (Fig.2). The slower decrease in the intensity of the line *O*, compared with the data in Ref.17, on going from $NbC_{0.995}$ to $NbC_{0.845}$, and the increase in its width, do not make it possible to assign this line to positions of niobium atoms with a complete environment up to the third coordination sphere, as was done in Ref.17. It is logical to assume that the line *O* in spectra *I–IV* (Fig.2) corresponds both to complete positions Nb_0^0 (Fig.4*a*) and to niobium atom positions containing vacancies only in the third coordination sphere, for example Nb_0^1 (Fig.4*b*), Nb_0^2, etc.

Fig.3, which shows the change in the form of the spectra with change in the degree of order, gives the ^{93}Nb NMR spectra obtained at frequencies of 21.5 MHz and 14.01 MHz for specimens with the composition $NbC_{0.83}$, subjected to thermal treatment under the three

conditions. Spectrum *I* for the specimen $NbC_{0.83}(a)$ contains one broad peak on either side of the line *O*; spectra *II* and *III* for the specimens $NbC_{0.83}(b)$ and $NbC_{0.83}(c)$ contain five peaks in addition to the line *O*. Spectra *IV* and *V* were obtained for the same specimens as spectra *I* and *II*, but at a lower frequency (Fig.3). The low relative intensity (~4%) of the line *O* (spectrum *II* in Fig.3), assigned to the positions Nb_0, and the approximately equal numbers of positions Nb_0 and Nb_2 in $NbC_{0.83}$ indicate that the peaks observed in spectrum *II* are associated chiefly with the positions Nb_1 (the peaks corresponding to the positions Nb_2 are not observed, in accordance with the second-order quadrupole effect).

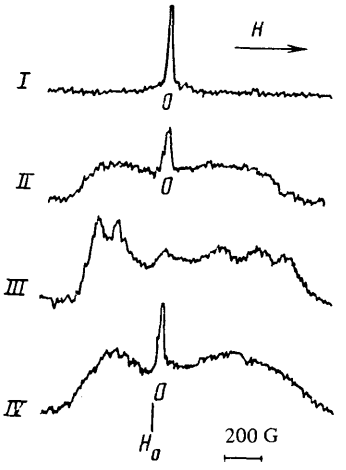


Figure 2. Change in the form of the ^{93}Nb NMR spectra with change in the composition of niobium carbide NbC_y (ν_0 = 21.5 MHz, H_0 = 20.69 kG); (*I*) $NbC_{0.995}$, (*II*) $NbC_{0.88}$ (*b*), (*III*) $NbC_{0.845}(b)$, (*IV*) $NbC_{0.75}(b)$.[34]

An analysis[33,34] of the frequency dependence of the positions of the peaks in the NMR spectra (spectra *II* and *V* in Fig.3) shows that the satellites can be only *O'* peaks, and the line of the central transition for them is the line *O*. The positions of the remaining peaks change with change in frequency, so that they are not satellites, but central transition lines. The broadening of the NMR spectra at low frequencies indicates that the contribution of quadrupole interactions is greater than that of the magnetic, so that the positions of the peaks *A*, *B*, *A'*, *B'* (spectrum *II*) and *A*, *B*, *A'*, *B'*, *C'*, *D'* (spectrum *V*) coincide with the positions of unique points of split central transition lines (the satellites of these lines are not observed, in accordance with the first-order quadrupole effect).

As a consequence of the asymmetry and high values of the electric field gradient, the positions of the peaks in the NMR spectra obtained at different frequencies change in a fairly complex fashion, so that in Refs.23, 33, and 34 a calculation was carried out making it possible to distinguish in spectra *II*, *III*, and *V* (Fig.3) the peaks assigned to different lines of the central transition. The calculation showed that in the NMR spectra of the carbide $NbC_{0.83}$ (Fig.3), in addition to the line *O*, it is possible to distinguish another four central transition lines. The positions of the unique points of the central transition lines and the corresponding parameters of the hyperfine interactions (the frequency of the quadrupole coupling ν_Q, the electric field gradient asymmetry parameter η_{as}, and the Knight shift *K*) are given in Table 1.

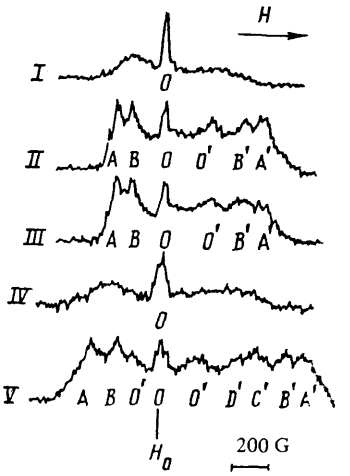


Figure 3. Influence of ordering on the ^{93}Nb NMR spectra of the carbide $NbC_{0.83}$; (*I*, *IV*) conditions *a*; (*II*, *V*) conditions *b*; (*III*) conditions *c* (*I*–*III*—ν_0 = 21.5 MHz, H_0 = 20.69 kG; (*IV*, *V*)—ν_0 = 14.01 MHz, H_0 13.46 kG).[33]

To assign the lines in spectra *II* and *V* (Fig.3) to various oppositions of the niobium atoms, a model calculation of the asymmetry parameter η_{as}, of the relative value of the frequency of the quadrupole coupling $\nu_Q/|q_C - q_\square|$ (where $|q_C - q_\square|$ is the absolute magnitude of the difference in the charges of the carbon atom and the vacancy, expressed in units of electron charge), and of the probabilities of the different positions of the niobium atoms $P_i^{disordered}$ and $P_i^{ordered}$ in the disordered and ordered states of $NbC_{0.83}$ respectively was carried out.[23,33,34] The results of the calculations[23,24] are given in Table 1. The large difference between $P_i^{disordered}$ and $P_i^{ordered}$ indicates that the NMR spectra of the disordered and ordered phases should differ considerably from one another. For example, for the disordered carbide $NbC_{0.83}$, the most probable positions are Nb_0^0 and Nb_0^1 (Fig.4) with a complete first coordination sphere, whereas for the ordered phase the most probable position is Nb_1^1 (Fig.4*b*), and there should be no niobium atom positions with a complete first coordination sphere.

In the comparison of the data on ν_Q and η_{as} obtained from the model calculation and from experiment, the authors cited[23] gave preference to the coincidence of the calculated and experimental values of the asymmetry parameters η_{as}^{calc} and η_{as}^{expt}. As a result of this comparison, they were able to find the experimental values of the hyperfine interaction parameters ν_Q, η_{as}, and *K* (Table 1) for different niobium atom positions.

By taking into account the environments of the niobium atoms with an accuracy up to three coordination spheres, the authors cited[23,33,34] were able to explain the presence of all the peaks in the ^{93}Nb NMR spectra of the carbide $NbC_{0.83}$. In the completely ordered $NbC_{0.83}$, only two types of position are possible, namely Nb_1^1 and Nb_1^2 (Figs.4*d* and 4*e*). The study of the carbides $NbC_{0.81}$ and $NbC_{0.88}$ showed that the nature of the short-range order in them is the same as in the monoclinic ordered phase Nb_6C_5 with space group $C2/m$.[37–40] Calculation of the Knight shifts showed that for niobium carbide, as for other non-stoichiometric compounds, the value of K increases with increase in the number of vacancies in the environment of the metal atom. The difference in the Knight shifts for different positions of the niobium atoms indicates a difference in the populations of their *d* orbitals for different immediate environments. Overall, the results obtained[23,33–36] indicate that the nature of the short-range order in niobium carbide, as in other non-stoichiometric compounds, is determined chiefly by the mutual repulsion of the vacancies in the non-metal sub-lattice.

2. The Study of Short-range Order by Diffuse Scattering

There are few published papers on the study of short-range order in non-stoichiometric compounds by diffuse scattering. Experimental data[45] on the intensity of the diffuse scattering of electrons by vanadium carbide $VC_{0.75}$ have been used[41–44] to calculate the parameters of the short-range order $\alpha(hkl)$ for the eight nearest coordination spheres of the non-metal sub-lattice; a vacancy was chosen as the centre of the coordination sphere. The results of the determination of the parameters α and the numbers of carbon atoms n_C and vacancies $n_\square$ in each coordination sphere are given in Table 2 (for comparison, the same quantities were calculated for the ordered phase V_6C_5 with a trigonal superstructure).

The data in Table 2 show that the nature of the distribution of the carbon atoms and vacancies in the non-metal sub-lattice of the carbide $VC_{0.75}$ differs considerably from the statistical distribution; for example, in the first two coordination spheres the number of vacancies is much smaller than that expected for the random distribution. With increase in the radius of the coordination sphere, the value of α oscillates, and its absolute magnitude gradually decreases. The results were attributed[43,44] to the mutual repulsion of the vacancies, and it was noted that analogous short-range order should be observed in niobium and tantalum carbides. The conclusion that there is similar short-range order in the non-stoichiometric monocarbides of the group V transition metals was also reached in Ref.46. According to Ref.46, it is impossible to obtain absolutely disordered (without short-range order) VC_y specimens with $y > 0.78$.

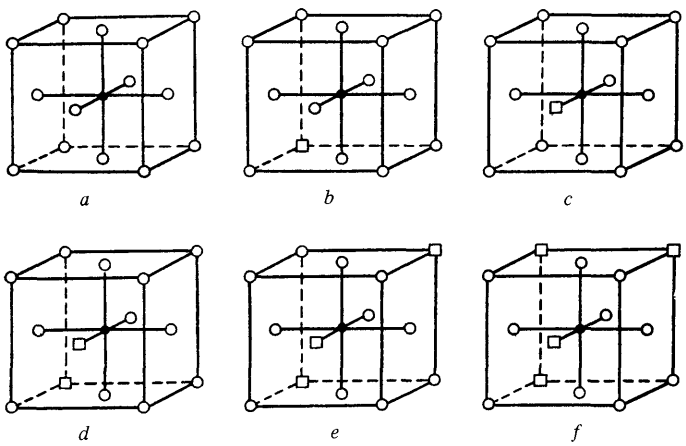


Figure 4. Most probable positions of the niobium atom in niobium carbide NbC*y*: (a) position Nb_0^0, (b) position Nb_0^1, (c) position Nb_1^0, (d) position Nb_1^1, (e) position Nb_1^2, (f) position Nb_1^3 (○—carbon atom, □—vacancy, ●—resonating niobium atom).

Table 1. Parameters of the ^{93}Nb NMR spectra of niobium carbide $NbC_{0.83}$ and the local environment of the niobium atoms.[23,33,34]

Nb position	Position symbol*	Position of vacancy**	Results of model calculations (Ref.23)				Unique points of the NMR spectrum***		Results of calculations from the NMR spectra (Refs.33, 34)			
			$\nu_Q/\lvert q_C-q_\square\rvert$, MHz	η_{as}^{calc}	$P_i^{disordered}$	$P_i^{ordered}$	$\nu_0=21.5$, MHz	$\nu_0=14.01$, MHz	ν_Q, MHz	η_{as}^{calc}	$\lvert q_C-q_\square\rvert$	K, %
Nb_0^0	*a*	—	0	0	0.09	0	*O*	*O*	0	—	—	−0.11±0.05
Nb_0^1	*b*	7	0.2	0	0.13	0	*O*, *O′*	*O*, *O′*	0.3±0.07	0	1.5	−0.11±0.05
Nb_0^2	—	7; 14	0.4	0	0.01	0	*O*	*O*	—	—	—	−0.11±0.05
Nb_0^2	—	7; 8	0.2	1.0	0.04	0	*O*	*O*	—	—	—	−0.11±0.05
Nb_0^2	—	7; 9	0.2	1.0	0.04	0	*O*	*O*	—	—	—	−0.11±0.05
Nb_1^0	*c*	1	1.05	0	0.10	0	*A*, *A′*	*A*, *A′*	1.9±0.3	0	1.8	−0.25±0.05
Nb_1^1	*d*	1; 7	1.05	0.2	0.07	0.66	*A*, *B′*	*A*, *B′*	2.0±0.3	0.2±0.05	1.9	−0.14±0.05
Nb_1^2	*e*	1; 7; 9	1.05	0.4	0.007	0.33	*B*, *O′*	*B*, *C′*	2.1±0.3	0.4±0.05	2.0	0.25±0.05
Nb_1^3	*f*	1; 7; 8; 9	1.05	0.6	0.001	0	*B*, *O′*	*B*, *D′*	2.2±0.3	0.5±0.10	2.1	0.50±0.10
Nb_2^0	—	1; 4	2.1	0	0.01	0	—	—	—	—	—	—

*See Fig.4.
**See Fig.1.
***See Fig.3.

Short-range order has been studied by the diffuse scattering of neutrons by the carbides $TiC_{0.76}$ and $NbC_{0.73}$.[47] The distribution of the intensity of the diffuse scattering of neutrons by single crystals of carbides with the composition indicated was measured at room temperature in the $(1\bar{1}0)$ plane of the reciprocal lattice in the range of change in the modulus of the diffraction vector $0.2\ Å^{-1} < 2\pi q < 4\ Å^{-1}$. Before the measurements, the single crystals of $TiC_{0.76}$ and $NbC_{0.73}$ were annealed in a vacuum for several days. The values obtained for the intensity of the diffuse scattering indicate that the atoms are displaced from the positions of the ideal undistorted lattice. A Fourier transformation was used[47] to determine the short-range order parameter α for the eight nearest coordination spheres of the non-metal sub-lattice of these carbides (Table 2). The data given in Table 2 show that the nature of the distribution of the vacancies in $TiC_{0.76}$ and $NbC_{0.73}$ is fundamentally the same, and, as in VC_y, is due to the mutual repulsion of vacancies. It was also noted[47] that the correlations in niobium carbide extend to more than nine coordination spheres. The results[47] show qualitative agreement with data obtained[46] in a study of NbC_y powders by the diffuse scattering of neutrons.

Table 2. Parameters of the short-range order and the distribution of the carbon atoms and vacancies in the carbide $VC_{0.75}$, the ideal ordered phase V_6C_5, and the carbides $NbC_{0.73}$ and $TiC_{0.76}$.

hkl	*N*	$VC_{0.75}$ (Ref.43)			V_6C_5 (Ref.43)			$NbC_{0.73}$ (Ref.47)			$TiC_{0.76}$ (Ref.47)		
		α	n_C	$n_\square$	α	n_C	$n_\square$	α	n_C	$n_\square$	α	n_C	$n_\square$
110	12	−0.178	10.6	1.4	−0.2	12	0	−0.095	9.6	2.4	−0.005	9.2	2.8
200	6	−0.260	5.7	0.3	−0.2	6	0	−0.275	5.6	0.4	−0.080	4.9	1.1
211	24	0.176	14.8	9.2	0.2	16	8	0.051	16.6	7.4	0.013	18.0	6.0
220	12	0.008	8.9	3.1	0	10	2	0.072	8.1	3.9	0.006	9.1	2.9
310	24	0.041	17.3	6.7	0	20	4	0.044	16.7	7.3	−0.003	18.3	5.7
222	8	−0.171	7.0	1.0	−0.2	8	0	−0.030	6.0	2.0	0.025	5.9	2.1
321	48	−0.070	38.5	9.5	−0.1	44	4	−0.020	35.7	12.3	−0.007	36.7	11.3
400	6	0.143	3.8	2.2	0.2	4	2	0.030	4.2	1.8	0.003	4.5	1.5

Notation: N is the number of sites in the coordination sphere (hkl).

The study of polycrystalline specimens of $ZrC_{0.80}$ and $ThC_{0.75}$ by the diffuse scattering of neutrons[46] made it possible to determine the correlations in the distribution of the vacancies in three coordination spheres (with a vacancy at the centre). According to these data, the first coordination sphere contains a small number of vacancies (smaller than that for the statistical distribution), the second coordination sphere contains no vacancies, and the third coordination sphere contains many more vacancies than for the random distribution ($\alpha_1 = -0.05$, $\alpha_2 = -0.20$, $\alpha_3 = 0.075$).

The diffuse scattering of electrons has been used to study short-range order in the lower carbides of vanadium and niobium V_2C and Nb_2C.[48] The short-range and long-range order in these compounds was related to the distribution of the interstitial atoms in regular rows $C-\square-C-\square-\ldots$ parallel to the c axis. Comparison of the experimental and calculated values of the intensity of diffuse scattering established the possible types of order in Nb_2C and V_2C.[48]

Overall, the available published data on short-range order in the non-metal sub-lattice of non-stoichiometric compounds indicate that the correlations in the distribution of the interstitial atoms and vacancies have been studied comparatively effectively only in the compounds of vanadium and niobium; the carbides of these metals have been studied in most detail. The nature of the short-range order in the non-metal sub-lattice of non-stoichiometric carbides is due mainly to the repulsion of vacancies. In the carbides of the group V transition metals, the sites of the first two coordination spheres (with a vacancy at the centre) are occupied chiefly by carbon atoms, whereas the vacancies are present mainly in the third coordination sphere; this type of short-range order corresponds to the distribution of the atoms in ordered phases of the type M_6C_5. In the carbides of the group IV transition metals, the nature of the short-range order is related to the fact that the second coordination sphere contains practically no vacancies, while the third coordination sphere contains large numbers of vacancies. The short-range order in the lower hexagonal carbides and nitrides M_2X is due to the formation of rows $X-\square-X-\square-\ldots$ directed along the c axis.

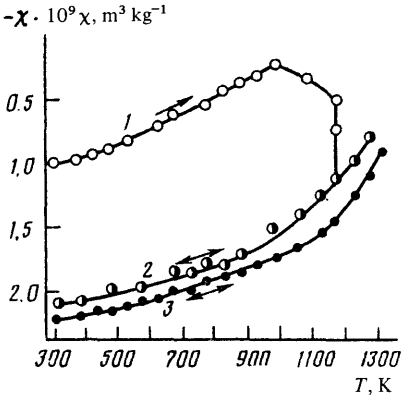


Figure 5. Influence of ordering on the magnetic susceptibility χ of niobium carbide $NbC_{0.83}$ (the arrows indicate the direction of the change in temperature): (1) quenched disordered carbide (2) carbide ordered during the measurement of the susceptibility, (3) annealed ordered carbide.[23,50]

3. The Study of Short-range Order by Magnetic Susceptibility

Magnetic susceptibility was first used to analyse the distribution of the atoms in a crystal and to determine short-range order in studies[23,49–51] of the non-stoichiometric niobium carbide NbC_y.

Measurements of the magnetic susceptibility χ of niobium carbide specimens with different compositions in the temperature range 300 – 1300 K showed that the value of χ depends on the nature of the thermal treatment of the carbide NbC_y ($0.81 \leqslant y \leqslant 0.88$). For specimens which were quenched from temperatures appreciably higher than the temperature of the disorder – order transition and which gave neutron diffraction patterns with no superstructural reflections, an abrupt decrease in χ was observed (Fig.5) to values characteristic of ordered specimens with the same composition, obtained by the methods of Refs.23 and 37. The neutron diffraction patterns recorded after the $\chi(T)$ measurements showed superstructural reflections, indicating that ordering of the structure takes place during the measurements. It was also found that the values of χ are the same for specimens containing the disordered and ordered phases simultaneously and for NbC_y specimens with the

same composition containing only the ordered phase, that is the susceptibility is independent of the concentration of the ordered phase. Since the production of long-range order is accompanied by the production of short-range order, the fact that χ is independent of the concentration of the ordered phase, and the change in χ on thermal treatment, indicate that the magnetic susceptibility is determined chiefly by the production of short-range and not long-range order.

The idea that short-range order has a definite influence on the magnitude of the magnetic susceptibility was confirmed by the calculation[23,49,50] of the short-range order parameters from experimental data.[23] The essential features of the calculation were as follows. Firstly, the $\chi(T)$ relationships for NbC_y specimens with different compositions in the disordered and ordered states were used to determine by the published method[49] the values of $P_i(y)$, the probabilities of existence in the NbC_y crystal of niobium atom positions with the i-th configuration of the carbon atoms, and the vacancies forming the immediate environment of the metal atom.

According to Refs.23, 49, and 50, for a correct description of the carbide MC_y in the composition range $1.0 \geqslant y \geqslant 0.80$ it is sufficient to consider only four positions: the position with a complete metal atom environment, having a probability P_0; the position with one vacancy in the octahedral environment of the metal atom, having a probability P_1; and positions with two non-adjacent and adjacent vacancies, having probabilities P_2 and P_3 respectively.

The short-range order parameter α_j in the j-th coordination sphere of the non-metal sub-lattice can be determined from the equation:[23]

$$\alpha_j = 1 - P^{(j)}_{C-\square}/P^{bin}_{C-\square}, \quad (4)$$

where $P^{(j)}_{(C-\square)}$ and $P^{bin}_{(C-\square)}$ are the probabilities of formation of the pair $C-\square$ in the compound being studied and in the completely disordered compound. For the carbide MC_y the binomial probability is $\lambda_{C-\square}P^{bin}_{C-\square} = 2y(1-y)$, and the actual probability of formation of the pair $C-\square$ in the j-th coordination sphere can be found from the known probability $P_i(y)$ using the equation:

$$\lambda_{C-\square}P^{(j)}_{C-\square} = \sum_i n_i^{(j)}\lambda_i P_i(y), \quad (5)$$

where $n_i^{(j)}$ is the relative fraction of $C-\square$ pairs in the j-th coordination sphere of the position of the metal atom with the i-th configuration; $\lambda_{C-\square} = 2$ is the multiplicity of the $C-\square$ pair; and λ_i is the multiplicity of the i-th configuration of the immediate environment of carbon atoms and vacancies round the metal atom (the multiplicity of a given group of atoms is the number of its equivalent configurations, which are brought into coincidence with one another by symmetry transformations). In the examination of the above four metal atom positions,

$$\lambda_{C-\square}P^{(1)}_{C-\square} = \lambda_1 P_1(y)/3 + 2\lambda_2 P_2(y)/3 + \lambda_3 P_3(y)/2$$

and

$$\lambda_{C-\square}P^{(2)}_{C-\square} = \lambda_1 P_1(y)/3 + 2\lambda_3 P_3(y)/3.$$

The calculation showed that for NbC_y specimens in the disordered state, the values of α_1 and α_2 are close to zero, whereas for the annealed specimens, the values of α_1 and α_2 are negative and differ considerably from zero; for example, for the annealed carbides $NbC_{0.88}$, $NbC_{0.83}$, and $NbC_{0.81}$, the parameters α_1 and α_2 have the values −0.064 and −0.040, −0.132 and −0.126, and −0.153 and −0.137 respectively. The negative values of α_1 and α_2 indicate the mutual repulsion of particles of the same kind, which also determines the nature of the short-range order in the non-metal sub-lattice of niobium carbide.

Magnetic susceptibility has also been used[52] to study the ordering in non-stoichiometric tantalum carbide TaC_y. The temperature dependence $\chi(T)$ for tantalum carbide specimens in the disordered and ordered states was similar to that observed[23,50] for niobium carbide. The experimentally measured magnetic susceptibility of tantalum carbide was used[52] to calculate the short-range order parameters. According to the calculation, the parameters in the first and second coordination spheres of the non-metal sub-lattice of ordered tantalum carbide are non-zero: $\alpha_1 = -0.086$ and $\alpha_2 = -0.054$ for $TaC_{0.83}$, and $\alpha_1 = -0.076$ and $\alpha_2 = -0.020$ for $TaC_{0.85}$.

For ideal ordered phases of the type $M_6C_5(MC_{0.83})$, $\alpha_1 = \alpha_2 = -0.20$,[49] in good agreement with the values obtained for $TaC_{0.83}$. The slight differences between the values of α_1 and α_2 calculated from the magnetic susceptibility and the limiting possible values of these parameters indicate that complete ordering was not achieved in the niobium and tantalum carbide specimens studied in Refs.49–52.

Overall, the results of the study of the short-range order in niobium and tantalum carbides by magnetic susceptibility[23,49–52] show good agreement with one another and with the results of NMR studies of the short-range order in non-stoichiometric carbides of the group V transition metals.

III. SHORT-RANGE ORDER IN CARBIDE SOLID SOLUTIONS

In the works discussed, the short-range order was studied in the non-metal sub-lattice of the non-stoichiometric compounds. The results of the study of the atom distribution in the metal sub-lattice of solid solutions of non-stoichiometric compounds of various transition metals are of considerable theoretical and practical interest.

The diffuse scattering of X-rays has been used repeatedly to study the short-range order in the metal sub-lattice of solid solutions formed by transition metal carbides with compositions close to the stoichiometric. In the opinion of Iveronova and Katsnel'son,[53] the most significant results of the study of short-range order in solid solutions M^1C-M^2C is the actual establishment of the fact that the distribution of the metal atoms in the sites of the metal sub-lattice is not random, and the detection of the influence of carbon on the nature of the correlations in the arrangement of the metal atoms.

The first studies of the local distribution of the atoms in the metal sub-lattice of the solid solutions NbC–TaC and ZrC–HfC with the equimolar composition were described in Refs.54–56. The absence of vacancies in the carbon sub-lattice and the similarity of the atomic radii of the metals replacing one another (Nb, Ta, Zr and Hf) made it possible to assume the absence of static distortions in the lattice of the solid solution. The short-range order parameters for the three nearest coordination spheres were calculated from the measured intensities of the diffuse scattering. For the first and second coordination spheres, the values of the short-range order parameters were found to be positive, and α_1 and α_2 increased with decrease in the temperature of quenching or annealing (Table 3). The positive values of α_1 and α_2 indicate that in the first and second coordination spheres of the metal atoms of a given kind, the concentration of metal atoms of the same kind is higher than that for the statistical distribution, that is there is short-range order involving short-range separation into layers. Short-range separation into layers has also been observed in Nb–Ta alloys.[57]

The short-range order parameter α_3 for the third coordination sphere is negative and close to zero, so that the correlations in the arrangement of the atoms in the metal sub-lattice apparently extend to only two coordination spheres. Additional annealing of the specimens of the solid solutions, and also the addition of 1 mole % WC, led to an increase in the correlations in the relative arrangements of the metal atoms.[54-56]

Table 3. Parameters of the short-range order in the metal sub-lattice of carbide solid solutions and in alloys.

Composition	T, K	Short-range order parameters			Refs.
		α_1	α_2	α_3	
$Nb_{0.5}Ta_{0.5}C$*	2000	0.058	0.025	$\leqslant 0$	[54]
$Nb_{0.5}Ta_{0.5}C$*	1800	0.089	0.049	$\leqslant 0$	[54]
$Nb_{0.5}Ta_{0.5}C$*	1500	0.120	0.071	$\leqslant 0$	[54]
$Nb_{0.5}Ta_{0.5}C$ + 1 mole % WC*	1800	0.11	0.10	0.02	[56]
$Nb_{0.5}Ta_{0.5}C$ + 1 mole % WC*	1500	0.14	0.13	0.04	[56]
$Nb_{0.5}Ta_{0.5}$	1600	0.13	0.09	0.02	[57]
$Nb_{0.5}Ta_{0.5}$*	1400	0.16	0.08	—0.04	[57]
$Zr_{0.5}Hf_{0.5}C$	2200	0.06	>0	$\leqslant 0$	[55]
$Zr_{0.5}Hf_{0.5}C$	1800	0.09	>0	$\leqslant 0$	[55]
$Nb_{0.5}Ti_{0.5}C$	2200	—0.06	—	—	[53,58,59]
$Nb_{0.75}Ti_{0.25}$	1500	0.066	0.103	—	[60]
$Nb_{0.5}Ti_{0.5}$	1500	0.063	0.047	—	[60]
$Nb_{0.25}Ti_{0.75}$	1500	0.091	0.017	—	[60]
$Ti_{0.5}Ta_{0.5}C$	2200	—0.06	—	—	[53.58.59]
$Ti_{0.5}Ta_{0.5}$	1500	0.19	—	—	[53.58.59]
$Ti_{0.5}Zr_{0.5}C$	—	0.07	—	—	[53]
$Ti_{0.5}Hf_{0.5}C$	—	0,03	—	—	[53]
$V_{0.5}Nb_{0.5}C$	2100	0.01	—	—	[53,58,59]
$V_{0.44}Nb_{0.56}$	—	—0,23	—	—	[53,58,59]
$V_{0.5}W_{0.5}C$	2100	0.03	—	—	[53,58,59]
$V_{0.65}W_{0.35}$	—	—0.10	—	—	[53,58,59]
$Ti_{0.5}W_{0.5}C$	2200	—0.06	—	—	[53,58,59]
$Ti_{0.01}W_{0.50}C_{0.99}$	2400	—0.09	0.03	0	[63]
$Ti_{0.77}W_{0.23}C_{0.99}$	2400	—0 07	0	0	[63]
$Ti_{0.94}W_{0.16}C_{0.99}$	2400	—0,06	0,02	0,01	[63]
$Ti_{0.01}W_{0.09}C_{0.99}$	2400	—0.05	—0,02	—0.02	[63]
$Ti_{0.58}W_{0.42}C_{0.94}$	2400	—0 06	0.04	0	[63]
$Ti_{0.58}W_{0.42}C_{0.86}$	2400	0,05	0.16	0.04	[63]
$Ti_{0.59}W_{0.41}C_{0.78}$	2400	0,07	0,15	0,03	[63]

*Specimens subjected to thermal treatment by annealing; in the other cases by quenching.

Diffuse scattering has been studied[58,59] in the solid solutions with the equimolar composition TiC—NbC, TiC—TaC, TiC—WC, VC—NbC, and VC—WC, and in the alloys Ti—Ta with the equiatomic composition, V—Nb (36 at.% Nb), and V—W (35 at.% W). The short-range order parameter α_1 is positive for the Ti—Ta alloys, and negative for the V—Nb and V—W alloys. For all the carbide solid solutions studied except VC—WC, $\alpha_1 < 0$; for VC—WC, $\alpha_1 > 0$. Comparison of the values of α_1 in the carbide solid solutions and in the corresponding metal alloys shows that in the solid solutions TiC—NbC, VC—WC, and TiC—TaC, the sign of α_1 is the opposite of that for the alloys Ti—Nb,[60] V—W, and Ti—Ta (Table 3).

The short-range order in TiC—WC solid solutions was studied in Refs.61—63. The intensity of the diffuse scattering of X-rays was measured using specimens with different compositions subjected to thermal treatment under slightly different conditions (sintering at different temperatures, quenching, gradual cooling in the furnace, etc.). According to the results, in all the specimens of the TiC—WC solid solutions with a complete carbon sub-lattice, $\alpha_1 < 0$, and for the second and third coordination spheres the parameters α_2 and α_3 are close to zero (Table 3). This means that the correlations in the arrangements of the titanium and tungsten atoms are observed at short distances within 1—3 coordination spheres. In all cases, additional annealing of the specimens led to an increase in the absolute magnitude of the short-range order parameters. States with a metal atom distribution close to the statistical distribution were not detected.

Increase in the tungsten concentration in the TiC—WC solid solutions is accompanied by an increase in the degree of short-range order in the first coordination sphere. The nature of the distribution of the metal atoms is influenced considerably by the carbon concentration. When the carbon concentration deviates from the stoichiometric, the short-range order parameters for the three nearest coordination spheres become positive (Table 3). At the same time, the nature of the diffuse scattering of X-rays by non-stoichiometric solid solutions indicates that there are two types of short-range order in their structures: with $\alpha_1 < 0$ and with $\alpha_1 > 0$. The authors cited[61-63] therefore suggested that in the non-stoichiometric solid solution $Ti_xW_{1-x}C_y$, in addition to the formation of segregations of the atoms of one metallic element, regions of short-range order with the structure typical of the stoichiometric solid solution are preserved.

IV. LOCAL DISPLACEMENTS OF THE ATOMS

In the disordered state, non-stoichiometric compounds are characterised by a random distribution of the interstitial atoms and vacancies in the sites of the non-metal sub-lattice, and therefore do not have the translational symmetry of the crystal with the stoichiometric composition. As a consequence of this random distribution, however, the probabilities of occupancy of the sites of the non-metal sub-lattice are equal, so that all these sites are crystallographically equivalent. In other words, in disordered non-stoichiometric compounds there is translational symmetry of a lattice of site occupancy probabilities.

Most non-stoichiometric compounds with wide homogeneity ranges have a highly symmetrical structure of the NaCl type, which is preserved for the disordered distribution of the interstitial atoms and vacancies. A result of the disordered distribution is the loss of the symmetry of the local environment of each atom. The distortion of the local symmetry leads in turn to static displacements of both the metal atoms and the interstitial atoms. The static displacements are the deviations of the atoms from the positions corresponding to the ideal basic structure of the compound, that is they represent the quantity $\mathbf{u}_n = \mathbf{R}_n - \mathbf{r}_n$, where $\mathbf{R}_n$ and $\mathbf{r}_n$ are the radius-vectors defining the position of the atom n in the real and ideal lattices respectively. Unlike the dynamic displacements, due to the thermal vibrations of the atoms, the static displacements result from the difference in the energies of the bonds between neighbouring atoms.

The cubic symmetry of disordered non-stoichiometric compounds allows only a spherically symmetrical distribution of the static displacements of the atoms, since otherwise the crystallographic equivalence of different sites of the crystal would be destroyed. In disordered non-stoichiometric compounds, the symmetrical distribution of the static displacements is ensured by the random distribution of the vacancies. By taking account of the radial distribution of the

static displacements and making use of the analogy with dynamic displacements, it is possible to examine the mean-square static displacements.

During ordering, the symmetry of the crystal is lowered, and is accompanied by a change in the symmetry of the local environment of the atoms (for the stoichiometric composition of the ordered phase, the symmetry of the local environment coincides with the crystal symmetry). Since in the ordered state the symmetry of the local environment is not cubic, ordering must be accompanied by static displacements of the atoms. The magnitude of the static displacements is different for the disordered and ordered states of a crystal, since the local environments of the atoms are different in these states.

The determination of the magnitude and direction of the static displacements for each atom in non-stoichiometric compounds with different structural states makes it possible to find the equilibrium positions, that is to determine the crystal structure more accurately and completely. Comparison of the values of the static displacements corresponding to different structural states can also be used to investigate possible mechanisms of phase transformations of the order–disorder type and to analyse the nature of the change in the inter-particle interactions in a crystal during ordering.

The principal methods for determining the displacements of atoms are by the diffraction of X-rays and thermal neutrons. There is no fundamental difference between these methods, since the elastic scattering of neutrons at the nuclei of the atoms and the scattering of X-rays on the static imperfections of the crystal are described by essentially identical equations and can be examined using the same theory.[64,65] At the same time, the difference in the parameters of the theory may lead to extremely significant methodological advantages.

The amplitudes of the scattering of X-rays by individual atoms are determined by the number of electrons in them, and increase regularly with increase in the atomic number of the element in the periodic system, whereas the amplitudes of the scattering of neutrons by the nuclei of different atoms change in irregular fashion. For non-stoichiometric compounds such as the transition metal carbides and nitrides, this means that in the scattering of X-rays, the main contribution to the intensity of the diffraction peaks will be made by the transition metal atoms, so that when X-ray diffraction is used to determine displacements, the information on the non-metal sub-lattice is practically completely lost. In neutron diffraction, the amplitudes of the atomic scattering of the neutrons by different components of non-stoichiometric compounds are of comparable magnitude (for example, for zirconium, hafnium, niobium, tantalum, carbon, and nitrogen, the amplitudes of the scattering of neutrons are 0.71×10^{-12}, 0.78×10^{-12}, 0.71×10^{-12}, 0.70×10^{-12}, 0.665×10^{-12}, and 0.94×10^{-12} cm respectively[66]). Thus when the diffraction of thermal neutrons is used, contributions to the intensity of the observed reflections are made by both the metal atoms and the non-metal atoms. The determination of displacements by neutron diffraction is in general more accurate than that by X-ray diffraction, since the amplitude of the scattering of neutrons is independent of the angle of scattering, and it is not necessary to introduce a correction for extinction; moreover, the absorption of neutrons by a substance is much less than the absorption of X-rays. Thus neutron diffraction is preferred for determining displacements in non-stoichiometric compounds of transition metals.

The decrease in the intensity of the diffraction lines is due to both dynamic (thermal) and static displacements of the atoms from the sites of the ideal crystal lattice, and in the absence of ordering these two factors bring about a decrease in intensity according to the same law.[64,67] In fact, the presence of dynamic displacements means that the positions of the atoms are time-dependent, but since the frequency of the scattered radiation is several orders of magnitude greater than the frequency of the thermal vibrations of the atoms, it can be assumed that the scattering takes place on stationary atoms occupying certain instantaneous positions. From this it follows that for the diffraction experiment there is no fundamental difference between dynamic and static displacements; it is necessary only to consider their superposition, as a result of which the intensity of the spectrum will depend on the sum of their mean-square values:

$$\langle U_{\Sigma}^2 \rangle = \langle U_{st}^2 \rangle + \langle U_{dyn}^2 \rangle. \quad (6)$$

The dynamic displacements can be separated from the total displacements, for example, by using the temperature dependence of the intensities of the diffraction lines.

At present, static displacements have been determined only for several transition metal carbides and nitrides; almost all the studies have been carried out only with compounds in the disordered state.

X-Ray diffraction has been used[68] to determine the displacements $< U_{\Sigma}^2 >$ of the atomic complex MX_y in the homogeneity ranges of the carbides of titanium, zirconium, and hafnium. The recording was carried out at room temperature, at which, in the opinion of the authors cited, the thermal vibrations of the atoms are small and the dynamic displacements can be neglected. Thus it was assumed[68] that $< U_{\Sigma}^2 > \simeq < U_{st}^2 >$. Increase in the defect character of the carbon sub-lattice was accompanied by a marked increase in the static distortions of the lattice (Table 4). The greatest static displacements are observed for titanium carbide; the magnitude of the displacements decreases on going to zirconium and hafnium carbides. Comparison of the nature of the change in the crystal lattice constants and the displacements with change in the composition of the carbides indicated that a sharper change in the crystal lattice constant with change in composition is accompanied by larger static distortions.

Neutron diffraction has been used[69] to determine the static displacements in the carbides of titanium, zirconium, vanadium, niobium, and tantalum. The effective mean-square displacements were found from the experimentally determined intensities of the diffraction reflections. For carbides MC with compositions close to the stoichiometric, the static distortions should be small, since the lattice is practically complete; thus for the stoichiometric compositions, $< U_{\Sigma}^2 > = < U_{dyn}^2 >$. Evidence in support of this is provided by the good agreement between the values obtained for $< U_{\Sigma}^2 >$ and the values of $< U_{dyn}^2 >$ calculated[70] from the elastic constants in the Debye approximation ($< U_{dyn}^2 >^{1/2}$ has the values 0.081 Å for TiC, 0.069 Å for ZrC, and 0.072 Å for NbC). The authors cited[69] assumed that the Debye temperature depends little on the composition of the carbides, and hence that the dynamic distortions of the lattice change little with decrease in the carbon concentration and that in a first approximation their dependence on the composition of the carbide MC_y can be neglected. This makes it possible to calculate the static displacements from the equation:

$$\langle U_{st\,MC_y}^2 \rangle = \langle U_{\Sigma\,MC_y}^2 \rangle - \langle U_{dyn\,MC}^2 \rangle = \langle U_{\Sigma MC_y}^2 \rangle - \langle U_{\Sigma MC}^2 \rangle. \quad (7)$$

The values obtained[69] for the displacements for titanium carbide were much lower than those obtained[68] by X-ray diffraction; the data[68,69] for zirconium carbide show better agreement (Table 4).

Neutron diffraction has been used[71] to determine the mean-square displacements of the atomic complex MN and the metal and nitrogen atoms, $< U_{\Sigma MN}^2 >$, $< U_{\Sigma M}^2 >$, and $< U_{\Sigma N}^2 >$, in the nitrides

$TiN_{0.98}$, $ZrN_{1.00}$, and $HfN_{0.98}$ with compositions close to the stoichiometric (Table 4). The results for titanium and zirconium nitrides agree satisfactorily with calculated data[72] obtained from the elastic constants in the Debye approximation ($<U^2_{dyn}>^{1/2}$ has the values 0.083 Å for TiN and 0.080 Å for ZrN).

Table 4. Mean-square displacements (Å) in non-stoichiometric compounds of transition metals MX_y.

Composition	$\langle U^2_{st\,MX_y}\rangle^{1/2}$	$\langle U^2_{cr\,MX_y}\rangle^{1/2}$	$\langle U^2_{\Sigma M}\rangle^{1/2}$	$\langle U^2_{\Sigma X}\rangle^{1/2}$	Refs.
$TiC_{0.82}$	—	0.160	—	—	[68]
$TiC_{0.66}$	—	0.184	—	—	[68]
$TiC_{0.50}$	—	0.199	—	—	[68]
$TiC_{0.96}$	0.084	—	—	—	[69]
$TiC_{0.86}$	0.104	0.065	—	—	[69]
$TiC_{0.81}$	0.119	0.087	—	—	[69]
$TiC_{0.65}$	0.142	0.118	—	—	[69]
$TiC_{0.96}$	0.103	—	0.084	0.109	[74]
$ZrC_{0.80}$	—	0.066	—	—	[68]
$ZrC_{0.70}$	—	0.120	—	—	[68]
$ZrC_{0.60}$	—	0.138	—	—	[68]
$ZrC_{0.97}$	0.075	—	—	—	[69]
$ZrC_{0.93}$	0.101	0.067	—	—	[69]
$ZrC_{0.87}$	0.110	0.080	—	—	[69]
$ZrC_{0.67}$	0.142	0.120	—	—	[69]
$ZrC_{0.63}$	0.147	0.126	—	—	[69]
$HfC_{0.90}$	—	0.080	—	—	[68]
$HfC_{0.70}$	—	0.091	—	—	[68]
$HfC_{0.60}$	—	0.095	—	—	[68]
$VC_{0.845}$	0.096	0.045	—	—	[69]
$VC_{0.814}$	0.106	0.063	—	—	[69]
$NbC_{1.0}$	0.081	—	—	—	[69]
$TaC_{1.0}$	0.091	—	—	—	[69]
$TiN_{0.98}$	0.089	—	0.078	0.100	[71]
$TiN_{0.98}$	0.105	—	0.081	0.096	[74]
$ZrN_{1.0}$	0.085	—	0.061	0.112	[71]
$HfN_{0.98}$	0.081	—	0.049	0.126	[71]
$TiC_{0.48}N_{0.51}$	0.107	—	—	—	[74]

The magnitude and direction of the relative static displacements of the atoms in the carbides $ZrC_{0.64}$,[46] $TiC_{0.76}$, and $NbC_{0.73}$ [47] have been determined by the diffuse scattering of neutrons. In $ZrC_{0.64}$, the zirconium atoms are displaced from the vacancies by 0.04 Å. In titanium and niobium carbides, the metal atoms are also displaced from the vacancy towards the carbon atom by 0.030 Å and 0.033 Å respectively, whereas the carbon atoms move away from one another (in the first coordination sphere of the non-metal sub-lattice, the distance between neighbouring carbon atoms increased by 0.011 Å in $TiC_{0.76}$ and by 0.006 Å in $NbC_{0.73}$).

The local displacements of the atoms situated round the carbon vacancy in NbC_y ($0.05 \leqslant y \leqslant 0.12$) have been determined[73] by an X-ray diffraction study of single crystals. To distinguish the dynamic and static displacements, the X-ray spectra of $NbC_{0.88}$ and $NbC_{0.93}$ were recorded at 299 K and 479 K. This made it possible to find the average Debye–Waller thermal factor for the temperature range indicated, equal to $2M = \ln(I_{479}/I_{299})$. According to the data obtained,[73] the magnitude of the dynamic displacements $<U^2_{dyn}>$ decreases with increase in the number of vacancies in the carbon sub-lattice of NbC_y, and can be described by the linear relationship

$$\langle U^2_{dyn}\rangle = 0.0027 - 0.005\,(1-y),\ \text{Å}^2. \qquad (8)$$

Since X-ray diffraction makes it possible to obtain information only on the metal sub-lattice, the authors cited[73] suggested that the vacancy is surrounded by six niobium atoms in the first and eight niobium atoms in the second coordination spheres, and that the displacement of the metal atoms in the subsequent coordination spheres and the displacements of the carbon atoms do not lead to a change in the X-ray diffraction patterns. It was also assumed that the vacancies are situated at an appreciable distance from one another, so that the position of the niobium atoms is influenced by only one vacancy. This assumption is applicable only for niobium carbide compositions close to the stoichiometric, and is not applicable to the $NbC_{0.88}$ specimen studied in Ref.73.

The static displacements of the niobium atoms for the first and second coordination spheres of a vacancy are $<U^2_{st}>_1 = 0.125$ Å and $<U^2_{st}>_2 = 0.009$ Å^2 respectively.[73] The directions of the displacements were also found; the niobium atoms in the first coordination sphere are displaced away from the vacancy, and those in the second coordination sphere are displaced towards the vacancy. Although the displacements of the niobium atoms in the second coordination sphere are much smaller than those in the first coordination sphere, the authors cited[73] assume that the displacements $<U^2_{st}>_2$ compensate the displacements in the first coordination sphere and lead to a decrease in the lattice constant of niobium carbide with increase in the concentration of vacancies. This interpretation of the experimental data appears doubtful, since in the work cited the coordinates of the carbon atoms were not determined, and the information on the positions of the niobium atoms is incomplete, that is there is practically no information on the crystal lattice constant.

The displacements $<U^2_{\Sigma MX_y}>$, $<U^2_{\Sigma M}>$, and $<U^2_{\Sigma X}>$ in titanium carbide $TiC_{0.96}$, titanium nitride $TiN_{0.98}$, and titanium carbide nitride $TiC_{0.48}N_{0.51}$ have been determined by neutron diffraction.[74] The authors cited give the values of the quantity $B = 8\pi^2 <U^2>/3$, from which the present authors calculated the values of the mean-square displacements $<U^2>$ (Table 4). The values of the displacements for titanium carbide and nitride show good agreement with the data of Refs.69 and 71, which were also obtained by neutron diffraction. In the study of titanium carbide in Ref.74, no deviations of the intensities of the diffraction reflections from the values calculated using the model of random displacements of the atoms from the positions of the ideal lattice were detected.

The displacements of the atoms in the homogeneity range of the disordered carbide NbC_y ($0.75 \leqslant y \leqslant 1.00$) have been studied in detail by neutron diffraction.[23,75,76] The presence of structural vacancies in non-stoichiometric niobium carbide brings about distortion of the symmetry of the local environment of the sites of the crystal lattice, and leads unavoidably to static displacements of both the atoms of the metallic matrix and the carbon atoms. When a special thermal treatment[23] ensuring a statistical distribution of the structural vacancies in the crystal lattice of the carbide is used, the symmetry of the carbide remains the same as that of the lattice of the defect-free carbide $NbC_{1.00}$, that is the disordered non-stoichiometric carbide NbC_y has an "average" highly symmetrical lattice, whose parameters change with change in composition. In this case the static distortions can be represented by the mean-square static displacements of the atoms, measured from the sites of this "average" lattice.

X-Ray diffraction[23] established that the concentration dependence of the cubic unit cell parameter of the disordered carbide NbC_y ($0.75 \leqslant y \leqslant 1.00$) is appreciably non-linear, with a point of inflection in the region of the composition $NbC_{0.83}$ (curve *1* in Fig.6).

In Refs.75 and 76, the mean-square static and dynamic displacements of the atoms were determined by neutron diffraction. The amplitudes of the scattering of neutrons by niobium and carbon atoms are of similar magnitude, and in this case the influence of the disordered displacements of the atoms on the diffraction effects can be taken into account using a Debye–Waller factor averaged over the atoms of different elements.[64,65,77] In a first approximation, the quantity M in the Debye–Waller factor can be regarded as a linear function of the displacements $\langle U_\Sigma^2 \rangle$:[77]

$$M = 2\pi^2 q^2 \langle U_\Sigma^2 \rangle / 3, \qquad (9)$$

where

$$q = |\mathbf{q}| = 2 \sin[\theta(hkl)]/\lambda$$

is the length of the vector of the reciprocal lattice.

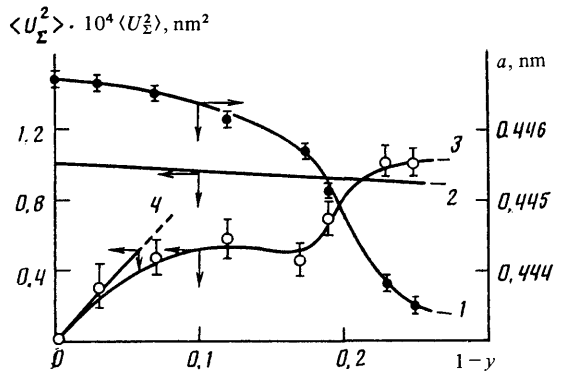


Figure 6. Changes in the crystal lattice parameter (1) and the dynamic (2) and static (3) mean-square displacements of the atoms in disordered niobium carbide NbC_y and the approximation of the static displacements (4) by Eqn.(11) in the range of low concentrations of vancancies.[76]

Measurement of the intensity of the diffraction peaks on the neutron diffraction patterns of the specimens of disordered NbC_y and construction of the $M = f(q^2)$ relationships, however, showed that they are non-linear at high values of q^2,[75,76] and the deviation from linearity takes place towards an increase in M for all niobium carbide specimens studied. Since a deviation of the $M = f(q^2)$ relationship from linearity is also characteristic of stoichiometric niobium carbide, the observed deviations were attributed[75,76] to the anharmonicity of the lattice vibrations of the atoms in niobium carbide. This conclusion agrees with the results of a study of the heat capacity of disordered niobium carbide,[78,79] where appreciable anharmonic effects were observed at $T \simeq 300$ K.

The contributions of the dynamic and static displacements of the atoms to $\langle U_\Sigma^2 \rangle$ were distinguished[75,76] using the concentration dependence of the dynamic displacements of the niobium and carbon atoms in NbC_y, found from data on the low-temperature heat capacity

$$\langle U_{dyn}^2 \rangle = [0.010 - 0.004(1-y)] \times 10^{-2} \text{ nm}^2, \qquad (10)$$

which indicates larger values of the dynamic displacements than in Ref.73. According to Eqn.(10), increase in the concentration of structural vacancies in niobium carbide is accompanied by a decrease in the magnitude of the dynamic displacements (curve *2* in Fig.6). This can be attributed to a change in the contribution of the displacements of the carbon atoms as a result of the decrease in the carbon concentration when the niobium carbide composition deviates from the stoichiometric.

Data on the total mean-square displacements of the atoms $\langle U_\Sigma^2 \rangle$ in NbC_y and the concentration dependence (10) of the dynamic displacements were used to determine the dependence of the mean-square static displacements $\langle U_{st}^2 \rangle$ on the niobium carbide composition (curve *3* in Fig.6). The magnitude of the static displacements increases when the niobium carbide composition deviates from the stoichiometric; a local minimum is observed for the specimen $NbC_{0.83}$. The appearance of this minimum is apparently due to the existence of short-range order in the arrangement of the carbon atoms and the vacancies; this could not be eliminated[75,76] even by quenching the specimens. The composition range in which the $\langle U_{st}^2 \rangle$ minimum is observed corresponds to the range in which, according to the data of Refs.23 and 37, the ordered monoclinic phase Nb_6C_5 is formed on prolonged annealing.

According to Ref.65, at low concentrations of defects and in the absence of correlations in the relative positions of the atoms, the dependence of the magnitude of the mean-square static displacements on the concentration of defects c bringing about static displacements has the form:

$$\langle U_{st}^2 \rangle = c(1-c)a^2 M_0 / 2\pi^2. \qquad (11)$$

Here,

$$M_0 = R^{-1}(dV/Vdc)^2,$$

where R^{-1} is the proportionality coefficient, a the unit cell parameter, and V the unit cell volume.

In NbC_y, the defects bringing about the static distortions are structural vacancies, so that $c = (1 - y)/2$. In Ref.76 it was shown that Eqn.(11) provides a good approximation to the experimentally observed static displacements only in the composition range $0.97 < y < 1.00$ (curve *4* in Fig.6). The value of R^{-1} determined for this composition range was found to be greater by approximately two orders of magnitude than that calculated[65] for interstitial alloys of non-transition metals. This indicates that in niobium carbide the static displacements of the atoms are greater than those in the alloys, and that strong localised interactions predominate. It also follows from Fig.6 that at high concentrations of defects, the theoretical values of the displacements become much larger than the experimental values. This is apparently related to the fact that in Ref.65, in the derivation of Eqn.(11), no account was taken of the overlap of

the perturbations created by the point defects. This overlap arises in NbC_y when the deviation from stoichiometry is large, and it unavoidably leads to a decrease in the rate of increase in the static displacements with increase in the concentration of vacancies.

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The material presented shows that in the last 10–15 years the study of the local distribution of the atoms in non-stoichiometric compounds of the transition metals has developed intensively. The results of the study of the structure of non-stoichiometric compounds and their solid solutions by diffraction, resonance, and other experimental methods show that the existence of short-range order in the relative arrangement of the atoms is an extremely widespread phenomenon in these substances, whereas it was previously assumed that the distribution of the interstitial atoms in non-stoichiometric compounds was completely statistical. The study of short-range order has been particularly successful using NMR, which is highly sensitive to small changes in the symmetry of the local environment of the atoms at which resonance is observed. The study of short-range order in non-stoichiometric compounds by magnetic susceptibility, which has not previously been used for this purpose, is also noteworthy.

An analysis of the experimental data shows that the nature of the short-range order in non-stoichiometric compounds is determined chiefly by the mutual repulsion of the vacancies or atoms of the same kind. This is indicated by the negative value of the short-range order parameters for the nearest coordination spheres of the non-metal sub-lattice. Studies of short-range order in the metal sub-lattice of carbide solid solutions have detected the existence of correlations in the relative arrangement of the metal atoms, and also the influence of the carbon concentration on not only the magnitude but also the sign of the short-range order parameter for the first coordination sphere.

The breakdown of the symmetry of the local environment of the atoms in non-stoichiometric compounds leads to static displacements of both the metal atoms and the interstitial atoms. The magnitude and direction of the static displacements are different for compounds in the disordered and ordered states. Comparison of the displacements corresponding to different structural states of a compound makes it possible to analyse the nature of the inter-particle interactions. Up to the present, however, experimental work in this direction has been restricted to the study of only disordered non-stoichiometric compounds.

Thus in the last ten years, the experimental study of the local distribution of the atoms in non-stoichiometric compounds has begun, but the problem of studying short-range order in these compounds has not been resolved. This applies particularly to the ordered phases of non-stoichiometric compounds, and also to non-stoichiometric compounds synthesised under thermobaric conditions, that is with the simultaneous application of high pressures and temperatures. The preparation of ordered phases by a redistribution of the atoms in the lattice, and the thermobaric synthesis of non-stoichiometric compounds, involving the filling of structural vacancies by atoms, provide new and promising methods for the directed synthesis of substances with specified properties. Studies of short-range order and the displacements of atoms may reveal the mechanisms of the transformations taking place in non-stoichiometric compounds, the nature of the interatomic interactions, and the influence of short-range order on the properties of these compounds. The principal experimental methods which should be used as widely as possible in the study of the phenomena of short-range order in non-stoichiometric compounds are the highly sensitive pulse NMR spectroscopy, the diffuse scattering of X-rays, neutrons, and electrons, and structural neutron diffraction.

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The Anisotropy of Molecular Magnetic Susceptibility and Its Structural-chemical Aspects

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Experimental data on the anisotropy of the magnetic susceptibilities of molecules and complexes have been summarised and systematised. A tensor additive scheme for the magnetic susceptibilities of the chemical bonds and groups of atoms in diamagnetic compounds has been developed. The application of the additive scheme to the analysis of the effects of the mutual influence of atoms, the problem of aromaticity, conformational structure, solvation, and complex formation has been examined.
The bibliography contains 177 references.

CONTENTS

I. Introduction 929
II. Methods for determining magnetic susceptibilities 929
III. The relationship between magnetic susceptibility and electric polarisability 931
IV. The tensor additive scheme 931
V. Effects of the mutual influence of atoms and the magnetic susceptibility tensor 934
VI. Magnetic anisotropy and problems of stereochemistry 936

I. INTRODUCTION

For a long time, molecular magnetochemistry, which studies the relationship between the magnetic properties and the structure of molecules, developed chiefly on the basis of a group of methods for determining average magnetic susceptibilities (MS). In the great majority of studies, with the exception of those devoted to the determination of the principal components of the molecular tensors of the MS in crystals, the anisotropies of the MS were not analysed. The intensive study of magnetic anisotropies has become possible as a result of the use in recent years of the molecular Zeeman effect in the gas phase,[1] the effects of linear magnetic birefringence in liquid media and the gas phase,[2-4] and NMR spectroscopy in strong fields.[5] The discussion of these methods in the literature is limited or non-existent, since the emphasis has been on the physics of the phenomena, and not on their application to chemical problems.

Unlike the average MS, the anisotropy is highly sensitive to the effects of intra- and intermolecular electronic interactions, and also to the relative orientation of functional groups. The experimental material which has now accumulated makes it possible to summarise published data on the determination of the anisotropic MS of molecules and the application of this fundamental electronic property to the solution of structural chemical problems.

II. METHODS FOR DETERMINING MAGNETIC SUSCEPTIBILITIES

The magnetic properties of an anisotropic molecule are described completely by nine quantities (k_{XX}, k_{XY}, k_{XZ}...k_{ij}), the set of which is called the MS tensor; from symmetry, $k_{ij} = k_{ji}$. The MS tensor can be represented in matrix form:

$$\begin{vmatrix} k_{XX} & k_{XY} & k_{XZ} \\ k_{YX} & k_{YY} & k_{YZ} \\ k_{ZX} & k_{ZY} & k_{ZZ} \end{vmatrix} \quad (1)$$

After reduction to the principal axes, the tensor becomes "diagonal":

$$\begin{vmatrix} k_{11} & 0 & 0 \\ 0 & k_{22} & 0 \\ 0 & 0 & k_{33} \end{vmatrix} \quad (2)$$

The invariants of a tensor are its trace and anisotropy. The trace is the sum of the diagonal elements, often characterised by the total (Σk_{ii}) or average ($\Sigma k_{ii}/3$) MS; their difference is the anisotropy (γ).[6-9] Methods for finding average MS have been described in detail in many reviews and monographs.[7,8,10-19] The data for approximately 800 compounds have been summarised in Ref.20.

Data on magnetic anisotropies have been analysed to a much smaller extent.

1. Microwave Spectroscopic Effects

The rotational Zeeman effect[1,21] in a gas consists of the splitting of the spectral lines into several components under the influence of a strong magnetic field. It has now become possible to measure and interpret the quadratic Zeeman effect, associated with the anisotropy of the MS. Measurement of the Zeeman effect is practically the only experimental method making it possible to separate the total MS into diamagnetic and polarisation paramagnetic components.[1,22] Since MS anisotropies are determined using the Zeeman effect in the gas phase, they can be regarded as standard. Unfortunately, a number of restrictions are imposed on the materials which can be studied by this method, and this reduces the range of substances which can be examined. These restrictions relate to the thermal stability of the specimens, the number of atoms other than hydrogen in the molecule (not more than 10), and the existence of a permanent electrical dipole moment in the molecule. The last restriction can be removed by studying the weak van der Waals complexes formed by the polar hydrogen halides with the centrosymmetric molecules

under investigation, for example acetylene[23] and cyclopropane.[24] Another approach involves partial deuteriation, used, for example, to determine the anisotropy of the MS of ethane (CH_3-CD_3).[25,26]

The anisotropies of the MS of the simplest molecules can also be determined by double electric resonance in molecular beams.[27,28]

2. The Molecular MS of Single Crystals

To find the principal MS of crystalline substances, it is sufficient to place a single crystal in a magnetic field in such a way that its lines of force coincide with one of the principal axes of the MS. Another approach is based on the tendency for a crystal of low symmetry suspended in a uniform magnetic field to orientate itself always in such a way that the axis corresponding to the MS of greatest absolute magnitude lies in the direction of the lines of force of the magnetic field.[7,8] The total MS tensor of a single crystal can be found by studying it in a non-uniform magnetic field.[8,12] A number of other methods can also be used to determine the principal MS of single crystals.[8]

At present, because of significant experimental difficulties, the tensors of only a limited number of molecules have been determined from data on the MS of crystals. Most of these data for diamagnetic materials have been tabulated;[7,29,30] values have also been obtained for a number of benzoic acids,[31-36] substituted nitrobenzenes,[37,38] and steroids,[39] and data on paramagnetic substances have been summarised;[40] data for lanthanide α,β-diketonates have also been published.[41]

It is assumed that the crystal packing has no influence on the molecular MS tensor, since the average MS of molecules in the liquid and solid phases are similar.[7] This assumption is not wholly correct, however. Rearrangement of the magnetic axes with preservation of their average value is always possible in principle. It would be strictly correct to compare the MS tensors of the same molecules in different states of aggregation. Special studies in this direction have not been carried out, and it has been reported only that these tensors are similar for various compounds, for example benzene and polynuclear hydrocarbons.[5] A correspondence between the results of measurements on crystals and measurements of the Cotton–Mouton effect in solutions has been reported for a number of aromatic compounds.[42,43] For compounds containing highly polar substituents, this question remains open. Thus for *p*-nitroaniline, satisfactory agreement is observed between the results of measurements of the Cotton–Mouton effect and measurements on crystals, whereas this agreement is not observed for *m*- and *p*-dinitrobenzenes.[44]

3. Magnetic Birefringence Effects

Data on magnetic birefringence in a transverse magnetic field can be used to determine the anisotropies of the MS in a gas, pure liquids, and solutions. Three types of magnetic birefringence are distiguished: in colloids[45] (the Majorana effect,[46] discovered in 1901), in diamagnetic molecules (the Cotton–Mouton effect, 1904),[2,3] and in paramagnetic substances, recently observed in solutions of lanthanide salts and complexes.[4,47]

Strange as it may seem, until recently, attempts to detect the paramagnetic effect were either unsuccessful[48] or declaratory in character;[49] in a number of cases the results contradicted one another,[49-51] and the superposition of other magneto-optical effects also took place.[50-57] Thus Elias[54] apparently observed in $Er(NO_3)_3$ the Voigt effect, that is birefringence in the characteristic absorption bands of the substance or in their direct proximity. In view of the tendency for Ce^{3+} salts to undergo hydrolysis,[58] the study of their aqueous solutions[52,53] apparently involved the Majorana effect in colloidal hydroxoaquo-complexes. An anomalously high magnetic birefringence effect was recorded in liquid oxygen.[55-57] Since however liquid oxygen is a liquid crystal[59] (and this state of matter is characterised by extremely large electro- and magneto-optical effects[60]), its high birefringence is due not to its paramagnetic character but to its liquid-crystal structure.

The molar constants of the diamagnetic ($_mC$) and paramagnetic ($_mP$) effects are described by expressions including the components of the tensors of the optical polarisability (b_{ij}), the diamagnetic susceptibility (k_{ij}), and the *g*-tensor:[47]

$$_mC = (2\pi N/45kT)\,[\Sigma(b_{ii}-b_{jj})(k_{ii}-k_{jj}) + 6\Sigma b_{ij}k_{ij}], \quad (3)$$

$$_mP = [(2\pi N/45kT(T-\delta)]\,(\mu^2/\Sigma g_{ii}^2)\,[(b_{ii}-b_{jj})(g_{ii}^2-g_{jj}^2) + 6\Sigma b_{ij}g_{ij}^2], \quad (4)$$

where N is Avogadro's number, k the Boltzmann constant, T the absolute temperature, δ the Weiss temperature correction to the Curie law in degrees absolute, and μ the magnetic moment in Bohr magnetons. Eqn. (4) clearly shows why the paramagnetic effect could not be observed in solutions of $FeCl_3$ and $Mn(NO_3)_3$ and in K and Na vapour;[48] the effect should be absent in purely spin systems. For systems with strong spin–orbit coupling, the paramagnetic effect is greater by 2–4 orders of magnitude than the Cotton–Mouton effect.[4,47] The latter can in principle be observed for any system both in the gas and in liquids and dilute solutions.[61-63] Unlike the constants of the electric analogue (the Kerr effect), the Cotton–Mouton constants are independent of the dielectric constant of the medium. This is indicated by $_mC$ data for aromatic compounds; the reliable determination of $_mC$ is possible not only for individual liquids ($_mC_l$) but also for solutions ($_mC_s$).[63,64] Further confirmation is provided by the identical values of the anisotropies of the MS of C_6H_6, alkyl halides, and CH_3CN, found by measuring the Zeeman effect in the gas phase and obtained from combined "solution" (Kerr effect) and "liquid" (Cotton–Mouton effect) data.[64] An exceptional place among other compounds is occupied by nitrobenzene, for which $_mC_l$ is almost twice $_mC_s$. This question is discussed in more detail in Section VI.

4. NMR Spectroscopy

Under the influence of strong magnetic fields (> 90 kG), the signals in high-resolution NMR spectra are split, the splitting being proportional to the magnitude of the anisotropy of the MS of the molecules and the square of the intensity of the applied field. This effect is due to the ordering of magnetically anisotropic molecules in liquids (solutions)[5] or gases,[65] which takes place as a result of the interaction of the quadrupole moment of the nuclei with the external field (the effect of dipole interaction is too small, and does not appear under these conditions). The most convenient object for the study of the NMR of partly oriented molecules is deuterium (^2H), since its quadrupole moment is sufficiently large for the splitting in real magnetic fields to be recorded, and at the same time is not so large that the broadening of the lines which it brings about makes it impossible to observe the splitting.[66] In very strong fields (~140 kG), the effect has also been studied at ^1H nuclei.[67,68]

The number of published studies using this approach is small, although it is undoubtedly promising. At present, this method is the only liquid-phase method which makes it possible to calculate all three components of the molecular MS tensor. Apart from halogenomethanes[69] and hydrogen cyanide,[70] this method has been used to find the anisotropies of the MS of only aromatic molecules[5,68,71-73] and anions.[73,74] It has also been applied to paramagnetic molecules.[67]

An alternative approach to the determination of the paramagnetic anisotropy of complexes is to solve the inverse problem, involving the analysis of the values of the pseudo-contact (dipole) contributions to the isotropic chemical shifts of ^{1}H and (or) ^{13}C due to the presence of the paramagnetic ions Co, Ni, and Ln.[75] Unfortunately, the application and accuracy of this method are restricted by a number of factors.[75,76] Nevertheless, it has been used successfully to determine the anisotropies of various complexes, in particular the bis-adducts of lanthanide dipivaloylmethanates with pyridine.[77] The components found in this way agree with the values previously obtained by direct magnetochemical measurements in single crystals.[41]

III. THE RELATIONSHIP BETWEEN MAGNETIC SUSCEPTIBILITY AND ELECTRIC POLARISABILITY

The electric polarisability and the magnetic susceptibility, which describe the deformability of the electron clouds of particles in magnetic and electric fields, are closely related to one another. This can be seen from the expressions

$$k = -(e^2/6mc^2)\Sigma\bar{r}^2, \quad b = (4/9na_0)\,|\Sigma\bar{r}^2|^2,$$

whose combination establishes the relationship between the MS (k) and the electric polarisability (b)[78]

$$k = -(e^2a_0^{1/2}/4mc^2)\,(nb)^{1/4}. \qquad (5)$$

Here, e is the charge of the electron, m its mass, n the total number of electrons in the system, $\Sigma\bar{r}^2$ the sum of the mean-square radii of the electron orbitals, and a_0 the Bohr radius. Eqn. (5) was obtained by Kirkwood, and is applicable for spherical atoms and monatomic ions. The main criticism of this equation is that the magnitude of the polarisability is determined chiefly by the electrons of the valence level, and not the inter levels, whereas all the electrons are equivalent with respect to precession in a magnetic field.[78] Nevertheless, for monatomic systems, good agreement is obtained between the results of experiment and calculation.[78] Kirkwood's model has also been developed for elliptical molecules and bonds. The magnetic susceptibility k_i oriented along the i axis is a function of the polarisability in two orthogonal directions, b_j and b_k:[79]

$$k_i = [-e^2(na_0)^{1/2}/8mc^2]\,[b_j^{1/2} + b_k^{1/2} - (b_j^{1/2} - b_k^{1/2})^2/(b_j^{1/2} + b_k^{1/2})]. \qquad (6)$$

For axially symmetrical systems, the anisotropy of the MS is described by the expression:[80]

$$\gamma = (-e^2/4mc^2)\,(na_0)^{1/4}\,[b_\perp\,(b_\perp^{1/2} - b_\parallel^{1/2})]/(b_\parallel^{1/2} + b_\perp^{1/2}), \qquad (7)$$

where $b_\parallel$ is the polarisability along the axis of cylindrical symmetry, and $b_\perp$ the perpendicular component. Eqn. (5) was subsequently applied to polyatomic molecules, and the difference between the calculated and experimentl MS was assigned *a priori* to the paramagnetic Van Vleck component.[78] Eqn. (6) has been used together with ^{1}H NMR spectroscopic data to estimate the MS and polarisability ellipsoids of the bonds C–C and C–H.[81] Verification of the practical applicability of Eqns. (5)–(7) for the case of the alkyl halides showed, however, that agreement with experiment is not observed at the level of the two invariants and the individual components of the tensor, including that for which the paramagnetic contribution should be small or non-existent.[80]

Analysis of the empirical $\Sigma k_i = f(\Sigma b_i)$ relationships shows that they are for the most part linear, although they are different for compounds of different classes.[82] Thus for a number of organophosphorus compounds containing saturated groups and P–O, P–S, P–Cl, P–H, P–C, P=O, and P=S bonds, the correlation has the form[64]

$$k_i = -0.180\cdot10^{-29} - 1.046(\pm0.037)\,\Sigma b_i\cdot10^{-5}.$$

Correlations with one another should probably be observed not only for the average characteristics of the bonds but also for their anisotropies. This is indicated by the fact that for chloro- and bromohydrocarbons the changes take place in the opposite sense.[80]

IV. THE TENSOR ADDITIVE SCHEME

The efficiency of magnetochemical studies of the structure of molecules depends significantly on the extent to which the additive principle relating molecular properties to the properties of individual atoms, bonds, and fragments is applicable to the anisotropic MS.

This principle is strictly observed for the average MS. This was first noted by Pascal, who pointed out that the difference in the MS of two neighbouring members of the homologue series of n-alkanes is constant. Having analysed the data for a large number of compounds, he concluded that the molar MS averaged over all directions and reduced to one molecule, $\chi_M = N\Sigma k_{ii}/3$, can be described by the relationship $\chi_M = \Sigma n_A\chi_A + \lambda$, where n_A is the number of atoms with MS χ_A in the molecule, and λ a constitutive correction which depends on the nature of the bonds between the atoms.[7,10,12,78] By analogy with the optical polarisabilities (refractions), this relationship can also be expressed in terms of bond characteristics.[78] The additive scheme of scalar MS was subsequently improved many times.[13,83-88] One of its most detailed versions is the system described in Ref.13. The values of the diamagnetic components for different ions are tabulated in Refs.7, 11, and 12. A theoretical validation of Pascal's empirical scheme was given in Ref.89.

In contrast to the scalar characteristics, the additivity of the MS tensor of molecules is not so obvious, except for aromatic hydrocarbons.[84,86,90] It has been shown that the diamagnetic component of the tensor retains additivity, but definite restrictions are imposed on the polarisation paramagnetic component, which changes with change in the symmetry of the orbitals on going from one molecular system to another.[1] It appears that in systems in which delocalised interactions (conjugation and hyperconjugation effects) predominate, so that the symmetry of a molecular orbital can be identified with the symmetry of the molecular framework, the paramagnetic part of the tensor may not be transferable. On the other hand, in molecules in which the interactions are localised (induction effects), that is in which the symmetry of the molecule is not related to the orbital symmetry, the MS tensor should remain additive, since in this case the molecular property is the sum of the properties of the individual bonds. This should be applicable for any electronic characteristic, including paramagnetism, which is independent of temperature.

Thus the MS tensor of 1,2-dibromoethane can be calculated sufficiently accurately from the MS of ethyl bromide (both compounds are characterised by only inductive interactions), in spite of the fact that these molecules have different symmetries and different positions of the centre of mass.[80] In contrast to this, the tensors of the molecules of benzyl bromide and 1,4-xylylene dibromide are not described by a single set of MS. In both compounds there is a strong interaction between a delocalised π-orbital of the aromatic ring and an antibonding orbital of the C−Br bond: $\pi_{ar}-\sigma^*(C-Br)$. In the case of benzyl bromide, the $\pi_{ar}-\sigma^*(C-Br)$ interaction as a result of the presence of the C−Br bond orientated unsymmetrically with respect to the ring leads to breakdown of the symmetry of the π-orbital as a whole, leading to the appearance of a super-additive contribution of the paramagnetic component in the direction perpendicular to the ring. In 1,4-xylylene dibromide, the CH_2Br groups in the *para*-positions increase the symmetry of the π-orbital of the aromatic ring delocalised over the unoccupied C−Br orbitals, and this "removes" the super-additive contribution of the Van Vleck component.[91]

It is convenient to examine the principles of the additivity of the MS tensors of the bonds and the solution of the inverse problem for a number of simple systems.

For a linear polyatomic molecule, the directions of the principal MS of the molecules and the bonds coincide. For non-linear molecules, the valence angles must be taken into account. For triatomic fragments AB_2 with an angle 2θ between the bonds in the system of principal axes, the following relationships apply:

$$k_1=2k_L\cos^2\theta+2k_T\sin^2\theta,$$
$$k_2=2k_L\sin^2\theta+2k_T\cos^2\theta,\quad k_3=2k_V. \tag{8}$$

Here and subsequently, k_1 is the MS directed along the axis of symmetry of the system, and k_2 and k_3 the MS in the other two orthogonal directions; k_L, k_T, and k_V are the longitudinal, transverse, and vertical MS of the bonds respectively. The solution of Eqn.(8) in the system of principal semi-axes of the MS ellipsoid of the bonds has the form:

$$k_V=k_3/2;\quad \gamma=k_L-k_T=(k_1-k_2)/(4\cos^2\theta-2). \tag{9}$$

similarly, for trigonal pyramidal molecules AB_3 (θ is the angle between A−B and the C_{3v} axis),

$$k_1=3(k_L\cos^2\theta+k_T\sin^2\theta),$$
$$k_2=k_3=1.5(k_L\sin^2\theta+k_T\cos^2\theta+k_V). \tag{10}$$

Assuming cylindrical symmetry of the bond ($k_T = k_V$), the solution of the system of equations (10) takes the form:

$$\gamma=k_L-k_T=(k_1-k_2)/1.5(3\cos^2\theta-1). \tag{11}$$

In the tensor additive scheme there is always a parameter whose value must be introduced arbitrarily or determined independently. This is related to the impossibility of separating the anisotropic molecular characteristics into components, even if the molecules contain bonds of only two types. Thus for example for ethane (and other alkanes), the irreducible combination of the anisotropies of the C−C and C−H bonds has the form:

$$\Gamma(C_2H_6)=\gamma(C-C)-2\gamma(C-H). \tag{12}$$

For mono-substituted methanes, the following relationship is applicable:

$$\Gamma(CH_3X)=\gamma(C-X)-\gamma(C-H)=\gamma(R-X). \tag{13}$$

For substituted benzenes which do not have axial symmetry but which contain a substituent with axial symmetry, the expression analogous to Eqn.(13) is converted into a system of equations including the anisotropy of benzene along the axis of symmetry $\Gamma(C_6H_6)$:

$$\Gamma_1(C_6H_5X)=\Gamma(C_6H_6)-1/2[\gamma(C-X)-\gamma(C-H)],$$
$$\Gamma_2(C_6H_5X)=-\Gamma(C_6H_6)/2+\gamma(C-X)-\gamma(C-H), \tag{14}$$

where Γ_1 and Γ_2 are the anisotropies of C_6H_5X perpendicular to and along the C−X bond respectively. In the more complex case of substituted ethylenes, the C=C bond is characterised by three different MS components, and the anisotropic part of the molecular tensor also includes combinations of the constant difference $\gamma(C-X)-\gamma(C-H)$.[92] This parameter in the calculation of the molecular tensor is reduced if the valence angles of the model systems and the systems being studied are close to one another. For clarity, this can be illustrated for the t-butyl derivative, whose molecular anisotropy is given by the expression

$$\Gamma(t\text{-}C_4H_9X)=\gamma(C-H)-\gamma(C-C)+\gamma(C-X). \tag{15}$$

On substitution of Eqns. (12) and (13) in Eqn.(15) and subsequent summation, γ(C−H) is eliminated:

$$\Gamma(t\text{-}C_4H_9X)=\Gamma(CH_3X)-\Gamma(CH_3X).$$

In contrast to methods involving the use of the Zeeman effect and NMR in strong fields, the method based on the measurement of the Cotton−Mouton effect makes it possible to determine the components of the MS only in the axially symmetrical approximation ($k_\parallel$ and $k_\perp$). The simultaneous examination of ${}_mC$ for several related compounds, for example homologues or molecules containing different numbers of identical functional groups, however, makes it possible to estimate the principal components of the MS for less symmetrical substituents. Thus in the determination of the three components of the MS tensor of the nitro-group it was assumed that γ(C−H) = 0, and a system of equations with three Cotton−Mouton constants for nitrobenzenes and *m*- and *p*-dinitrobenzenes was examined. After substituting the known numerical values of the fundamental constants and the tensors of the electric polarisability and the anisotropy of the MS of the benzene ring with allowance for the geometry of the molecules, expressions were obtained for ${}_mC$ as functions of the anisotropies $\gamma_1 = k_1-k_2$ and $\gamma_2 = k_1-k_3$ (k_1 is directed along the C−NO_2 symmetry axis, and k_3 is normal to the plane of the group):

$${}_mC(NB)=(-2.57\gamma_1+12.40\gamma_2+131.2\cdot10^{-29})/48.08\cdot10^{14},$$
$${}_mC(m\text{-}DNB)=(-15.75\gamma_1+37.8\gamma_2+199\cdot10^{-29})/48.08\cdot10^{14}. \tag{16}$$

Using the known experimental values of ${}_mC$ for NB, *m*-DNB, and *p*-DNB (3.83×10^{-15} emu, 6.00×10^{-15} emu, and 4.70×10^{-15} emu respectively), it can readily be shown that $\gamma_1 = 0.8\times10^{-29}$ cm^3 and $\gamma_2 = 2.7\times10^{-29}$ cm^3.[93] The values of γ_1 and γ_2, and also of k_l for the nitro-group, given in Ref.94, are incorrect, because of an error in writing the system of equations (16). Similarly, the triaxial MS tensor of the carbonyl group was calculated using the values of ${}_mC$ for acetone and cyclohexanone[95] and the tensors of the C=C bond (the corresponding values for *cis*- and *trans*-dichloroethylenes[92]) and the $C_{ar}-O$ bonds (the constants for different substituted anisoles[96]). The tensor characteristics of the bonds of a number of saturated and unsaturated molecules have been found from data on the Zeeman effect by averaging the MS of these bonds by the least-squares method.[1] The assumptions that the anisotropy of the MS of the C−H bond is independent of the hybridisation of the C atom and that k_T and k_V are equal, and also the differences in the valence

angles at the C_{sp^3}, C_{sp^2}, and C_{sp} atoms, made it possible to distinguish $\gamma(C-H)$. This quantity was found to be negative, as confirmed by the data in Ref.92, although it does not agree with Ref.97.

An approach based on the isotropic character of the C—H bonds is widely used in the analysis of tensor electric polarisabilities;[79] it facilitates considerably the calculation of the anisotropic molecular characteristics, since a knowledge of the spatial positions of the C—H bonds in the molecular structures and confirmations is not required. The relative values of the tensor additive MS of bonds, based on the assumption that the C—H bonds are isotropic, are given in Table 1. The values were calculated by the present authors from published data on the molecular ellipsoids or anisotropies of the MS obtained by the above methods. The Table does not include the data from Ref.98, which are erroneous.[43]

Table 1. Tensor additive magnetic susceptibilities of different bonds and groups, calculated assuming that the C—H bonds are isotropic ($k_t(\gamma) \times 10^{29}$, cm^3).

Bond, group	Model compound	$-k_L$ or $-k_1$, (γ)	$-k_T$ ($-k\gamma$) or $-k_2$ ($-k_3$)	Method	Refs.
C—C	n-alkanes	0.76	0.54	SC	[99]
C—C	aliphatic acids with a long chain	0.83	0.50	CM (l)	[100]
C—C	ethane	0.88	0.48	CM (g)	[61]
C—C	isobutane	0.91	0.46	Z	[101]
C—C	–	0.92*	0.45*	Z*	[1]
C—C	cyclohexane	0.93	0.45	CM (l)	[102]
C—C	ethane	1.21	0.31	Z	[25]
C—C	ethane	1.26	0.29	CM (g)	[103]
C—C	ethane	1.28	0.28	Z	[26]
C=C	trimethyl- and 1,2-dichloroethylenes	0.57	1.23 (3.09)	CM (l)	[92]
C=C	–	0.35*	0.44 (2.50)*	Z*	[1]
C≡C	–	2.83*	2.13*	Z*	[1]
C≡C	acetylene + HCl	2.82	2.14	Z	[23]
C_3	cyclopropane + HCl	2.2	2.2 (3.7)	Z	[24]
C_3	cyclopropane	2.07	2.07 (4.0)	CM (g)	[104]
C_6H_5	benzene	5.6	5.6 (14.5)	CM (g)	[105]
C_6H_5	benzene	5.56	5.56 (14.6)	CM (l)	[43]
C_6H_5	benzene	5.47	5.47 (14.8)	NMR (l)	[5]
C_6H_5	benzene	5.37	5.37 (15.0)	CM (s)	[62]
C_6H_5	benzene	5.27	5.27 (15.2)	SC	[106]
C_6H_5	benzene	5.1	5.1 (15.5)	CM (s)	[43]
C_6H_5	benzene	5.07	5.07 (15.6)	Z	[1]
C_6H_5	benzene	5.07	5.07 (15.6)	CM (s)	[102]
C_6H_5	benzene	4.87	4.87 (16.0)	NMR (s)	[5]
C_{ar}-CH_3	durene	2.31	1.89 (2.12)	SC	[43]
C_{ar}-CH_3	toluene	1.54	2.32	CM (s)	[43]
C_6H_5—C	toluene	5.6	5.2 (16.0)	CM (s)	[43]
C_6H_5—C	benzyl halides	4.9	7.9 (13.9)	CM (s)	[91]
C_{sp}—CH_3	methylacetylene, acetylene	2.80	2.20	Z	[106]
C_{sp}—CH_3	acetonitrile, hydrogen cyanide	2.2	1.7	Z	[106]
C—F	methyl fluoride	1.77	0.41	Z	[106, 107]
C—F	methylene fluoride	0.94	0.60 (0.62)	Z	[106]
C—F	fluoroform	(0.2)	—	Z	[107]
C_{ar}-F	fluorobenzene	1.65	0.93	CM (s)	[96]
C_{ar}-F	fluorobenzene	1.73	1.13 (0.64)	Z	[1]
C_{ar}-F	fluorobenzene	1.78	1.16 (0.40)	Z	[108]
C_{ar}-F	fluorobenzene	1.43	1.33 (0.7)	NMR (s)	[71]
C_{ar}-F	fluorobenzene	0.33	1.04 (1.31)	NMR (l)	[71]
C_{sp}—F	fluoroacetylene	1.52	1.36	Z	[106]
C_{sp}—F	fluorine cyanide	1.62	1.62	Z	[107]
C—Cl	methyl chloride	4.06	2.74	Z	[107]
C—Cl	1,2-dichloroethane	4.16	3.06	CM (l)	[80]
C—Cl	isopropyl chloride	4.39	2.95	CM (l)	[80]
C—Cl	t-butyl chloride	4.55	2.88	CM (l)	[80]
C—Cl	methylene chloride	4.59	2.55	CM (l)	[80]
C—Cl	methylene chloride	4.20	2.76 (2.65)	NMR (s)	[69]
C—Cl	chloroform	4.75	2.21	NMR (s)	[69]
C—Cl	chloroform	4.43	2.38	CM (l)	[80]
C_{sp^2}—Cl	1-chlorocyclohexene	3.89	2.96	CM (l)	[92]
C_{sp^2}—Cl	1,2-dichloroethylene	4.16	2.82	CM (l)	[92]
C_{ar}-Cl	chlorobenzene	3.63	3.13 (2.4)	NMR (s)	[71]
C_{ar}-Cl	chlorobenzene	2.35	2.53 (4.15)	NMR (l)	[71]
C_{ar}-Cl	chlorobenzene	3.97	2.06	CM (s)	[43]
C_{ar}-Cl	p-dichlorobenzene	3.88	1.56 (2.10)	SC	[43]
C_{sp}—Cl	chlorine cyanide	3.55	2.95	Z	[109]
C_{sp}—Cl	chloroacetylene	4.04	3.20	Z	[106]
C—Br	methyl bromide	5.60	4.20	Z	[107]
C—Br	ethyl bromide	5.60	4.20	CM (s)	[80]
C—Br	isopropyl bromide	5.73	4.14	CM (s)	[80]
C—Br	t-butyl bromide	5.83	4.09	CM (s)	[80]
C—Br	methylene bromide	6.46	3.77	CM (s)	[80]
C—Br	methylene bromide	6.08	4.15 (4.0)	NMR (s)	[69]
C—Br	bromoform	6.9	3.1	NMR (s)	[69]
C—Br	bromoform	6.41	3.80	CM (s)	[80]
C_{ar}-Br	bromobenzene	5.4	4.8 (3.9)	NMR (s)	[71]
C_{ar}-Br	bromobenzene	4.1	4.4 (5.7)	NMR (l)	[71]
C_{ar}-Br	bromobenzene	5.64	3.72	CM (s)	[43]
C_{ar}-Br	p-dibromobenzene	5.45	3.24 (3.47)	SC	[43]
C_{sp}—Br	bromoacetylene	5.47	4.50	Z	[106]
C_{sp}—Br	bromine cyanide	5.30	4.47	Z	[106]
C—I	methyl iodide	8.55	6.72	Z	[107]
C—I	methyl iodide	8.40	6.79	CM (s)	[43]
C—I	ethyl iodide	8.42	6.78	CM (s)	[43]
C—I	isopropyl iodide	8.50	6.75	CM (s)	[43]
C—I	t-butyl iodide	8.67	6.66	CM (s)	[43]
C—I	methylene iodide	9.1	6.1 (5.9)	NMR (s)	[69]
C—I	iodoform	10.73	4.05	NMR (s)	[69]
C_{sp}—I	iodine cyanide	8.13	6.63	Z	[106]
C—CN	acetonitrile	3.65	1.98	CM (l)	[93]
C—CN	acetonitrile	3.70	1.96	Z	[1]
C_{ar}-CN	benzonitrile	2.44	2.17	CM (s)	[93]
C_{ar}-CN	benzonitrile, m-dicyanobenzene	1.34	5.05 (0.4)	CM (s)	[93]
C—N	1,3,5-trimethylhexanhydro-1,3,5-triazine	1.15	0.57	CM (l)	[44]
C_{ar}-N	aniline	1.3	0.8 (—0.5)	NMR (s)	[71]
C_{ar}-N	anilines	1.63	1.63 (—1.66)	CM (s)	[44]
C_{ar}-N	N,N-dimethylanilines	1.93	—0.27 (—0.06)	CM (s)	[44]
C_6H_5—N	anilines	6.7	6.7 (13.9)	CM (s)	[44]
C_6H_5—N	N,N-dimethylanilines	7.0	4.8 (15.5)	CM (s)	[44]
C_{ar}-NO_2	nitrobenzene, m-dinitro- and p-dinitrobenzenes	0.53	1.33 (3.23)	CM (s)	[93]
C_{ar}-NO_2	nitrobenzene	—0.1	0.9 (4.3)	NMR (s)	[72]
C_{ar}-NO_2	m-dinitrobenzene	0.9	—0.1 (4.3)	NMR (s)	[72]
C≡N	hydrogen cyanide	2.97	1.77	Z	[1]
C≡N	deuterium cyanide	2.70	1.90	NMR (s)	[70]
C—O	dimethyl ether	0.63	0.8 (0.3)	Z	[1]
C—O	dioxan	0.96	0.40	CM (s)	[96]
C_{ar}-O	anisole, p-dimethylanisole	1.07	—0.28 (1.72)	CM (s)	[96]
C_{ar}-O	o,o-dimethylanisole, p-chloro-o,o-dimethylanisole	2.18	0.14 (0.18)	CM (s)	[96]
C=O	formaldehyde	—0.94	0.16 (1.12)	Z	[106]
C=O	–	0.25*	0.09 (2.0)*	Z*	[1]
C=O	acetone, cyclohexanone	—0.25	—0.46 (1.22)	CM (s)	[96]
C_2C=O	acetone, cyclohexanone	0.92	1.13 (1.22)	CM (s)	[96]
C_2O	oxiran	1.25	0.30 (2.35)	Z	[1]
C—S	dimethyl sulphide	1.83	1.13 (1.63)	Z	[1]
C=S	–	—0.84*	1.36 (5.06)*	Z*	[1]
C≡P	–	5.37*	3.97*	Z*	[1]
P—O	1,3,2-dioxaphosphorinanes	(—2.55)	—	CM (l)	[64]
P—F	phosphorus trifluoride	(0.47)	—	Z	[64]
P—Cl	phosphorus trichloride	5.25	1.51	CM (l)	[64]
P=O	phosphorus oxide fluoride	(—0.05)	—	Z	[64]
P=O	phosphorus oxide chloride	1.71	2.15	CM (l)	[64]
P=O	2-oxo-1,3,2-dioxaphosphorinanes	(1.0)	—	CM (l)	[110]
P=S	phosphorus oxide chloride sulphide	6.36	4.22	CM (l)	[110]
P=S	2-thio-1,3,2-dioxaphosphorinanes	(—2.34)	—	CM (l)	[110]

Table 1 (continued).

* Calculated from averaged data.[1]

Note: SC = method based on measurements of the MS of single crystals; CM = method based on the use of the Cotton—Mouton effect; Z = method based on the use of the Zeeman effect; NMR = NMR of partly orientated molecules; the state of aggregation of the substance is indicated in brackets: g = gas, l = liquid, s = solution.

The absolute values of the bond and group anisotropies are required in the analysis of intramolecular magnetic parameters such as the chemical shifts or the cones of the magnetic shielding in NMR spectroscopy.

NMR makes it possible to use the values of the chemical shifts (usually of ^{1}H and ^{13}C) to estimate the absolute anisotropies of individual bonds and groups of atoms. This estimation is based on the dependence of the shielding constants of the protons on a number of electronic properties, including the anisotropy of the MS of the fragments adjoining the proton. In existing models, the anisotropic fragment is represented as a point,[111] a one-dimensional dipole[97] or, which is most correct, as a closed contour of finite dimensions with electrons circulating in it.[112,113] It is convenient to carry out specific calculations for a known molecular geometry using the published magnetic iso-shielding map.[113] Here it is also necessary to take into account the contribution of the electrostatic component.[20] To eliminate effects transferred along the chain of atoms, the differences in the chemical shifts of geminal protons or protons in configurational (conformational) isomers are usually examined. It should be emphasised that the approach described is extremely approximate, and includes a number of assumptions, such as the localisation of the centre of the magnetic dipole or the maximum electron density of the substituent; in addition, there arise the questions of the applicability of the models of the dipole and non-dipole approximations used and allowance for intramolecular electronic interactions (induction, conjugation, hyperconjugation, and the field effect). Nevertheless, NMR spectroscopy is apparently the only method which makes it possible, particularly when combined with magneto-optical data, to separate the combinations of the anisotropies of the MS of bonds. This method was used, for example, to determine the anisotropy of the MS of the lone pair of electrons of the phosphorus atom.[110] The tensor additive characteristics of various chemical bonds and groups, found using the above models, are given in Table 2. It is emphasised that the data in Table 2 must be regarded as tentative, since they were obtained by different authors in different approximations. It is also obvious that the values of the anisotropic MS in Tables 1 and 2 cannot be compared without appropriate recalculation.

Table 2. Magnetic anisotropy of bonds and groups from NMR data (10^{29} γ, cm^3).

Bond, group	γ_i (γ_2)	Refs.	Bond, group	γ_i (γ_2)	Refs.
C—H	0	[81]	C—O	0.5	[125]
C—H	0	[114]	C=O	0.8 (1.0)	[126]
C—H	0—0.25	[115]	C=O	1.28 (—0.17)	[126]
C—H	0—0.25	[116]	C=O	—0.83 (—1.0)	[126]
C—H	0.5	[99]	C=O	—0.4 (1.06)	[126]
C—H	0.754	[117]	C=O	2.48 (3.68)	[117]
C—H	1.351	[117]	C=O	2.79 (3.97)	[117]
C—H	—0.7	[92]	C≡N	—5.64	[127]
C—C	0.17	[81]	C—F	—1.0	[128]
C—C	0.25—0.5	[116]	C—Cl	0.5	[125]
C—C	0.32—0.62	[115]	C—Cl	—1.3	[128]
C—C	0.55	[118]	C≡CH	—5.65	[127]
C—C	0.65	[119]	C≡CCl	—6.15	[127]
C—C	0.67	[99]	C≡CBr	—6.13	[127]
C—C	0.73	[114]	C≡Cl	—5.81	[127]
C—C	0.83	[120]	C_3H_6	—3.5	[129]
C—C	1.17	[121]	C_3H_6	—2.5	[130]
C—C	1.126	[117]	C_3H_6	—1.83	[131]
C—C	2.314	[117]	C—NO_2	—7.5 (0.5)	[132]
C=C	—1.2 (—1.21)	[117]	S—O	1.0	[133]
C=C	—1.37	[122]	S—O	2.24	[134]
C≡C	—1.8 (2.5)	[92]	Cr(CO)	—4.08	[135]
C≡C	—1.97	[123]	Mo(CO)	—4.69	[135]
C≡C	—2.74	[124]	W(CO)	—5.32	[135]
C—O	0.65	[119]	LPE*	0.27	[110]

*LPE = lone pair of electrons of the phosphorus atom.

The paramagnetic susceptibility of complexes and ions is determined by the number of unpaired electrons and by the symmetry and strength of the ligand field.[9,136] Since the orientational paramagnetism is characteristic of a specific ion, the concept of additivity of the paramagnetic susceptibility tensor for mononuclear systems loses its meaning, and the primary problem becomes its transferability from one type of molecule to another. The transferability of the average characteristic of the tensor in the 4*f* lanthanide elements is well known (their magnetic moments are practically independent of the environment[12]), but it is greatly restricted for transition metal complexes. The individual components of the tensor, and the anisotropy, are more sensitive to the environment of the ion, although judging from paramagnetic birefringence data, satisfactory transferability of the tensor paramagnetic characteristics is also observed in various inner-complex compounds of the lanthanides with different degrees of coordination.[47,137,138] The dependence of the components of the paramagnetic susceptibility tensor on the symmetry of the crystal field has been clearly demonstrated.[139] The quantitative calculations are based on the fundamental theory of Van Vleck.[9] Examples of the calculation of the anisotropies of the lanthanides are given in Refs.76 and 136. One of the corresponding calculation programs is described in Ref.140.

V. EFFECTS OF THE MUTUAL INFLUENCE OF ATOMS AND THE MAGNETIC SUSCEPTIBILITY TENSOR

1. Magnetic Properties and the Nature of the Chemical Bond

The dependence of the anisotropy of the MS of a chemical bond on its nature (symmetry, multiplicity, and the hybridisation of the atoms forming it) and on the effect of neighbouring substituents has not been studied systematically. Sufficient experimental material (see Table 1) has now been accumulated, however, to make possible a number of simple generalisations.

1) Most bonds with cylindrical symmetry, whether single (C—C, C—F, C—Cl, C—Br, C—I, C—N, C—O, C—S, P—Cl, P—O, N—H) or multiple (C≡C, C≡N, C≡P, P=S), show maximum diamagnetism in the longitudinal direction, that is negative anisotropy.

2) For substituents which do not have axial symmetry, a decrease in the diamagnetism in the plane of the fragment and an increase in the vertical component along the axes of the *p* electrons (P=O, C=S, C=C, C—NO_2) are observed, as in aromatic systems.

3) The absolute magnitude of the anisotropies of the MS of bonds between atoms which have similar electronic structures (C—O and C—S; C=O and C=S; C=N and C=P; C—F, C—Cl, C—Br, and C—I) increases with increase in the atomic number of the element.

The influence of the nature of atoms in the same period of the periodic system does not show clearly defined regularities.

4) The magnetic anisotropy of a bond is not constant, and depends on the nature of the surrounding substituents. Thus its absolute magnitude increases with increase in the electronegativity (methyl and methylene halides and haloforms) and size of neighbouring groups of atoms (halogen derivatives).

The influence of the effects of the immediate environment, in particular the change in the double-bond character, can be clearly seen in the series of C–O bonds on going from aliphatic to aromatic ethers and carbonyl derivatives. In dioxan, as in 2,6-dimethylanisole, where as a consequence of the orthogonality of the methoxy-group there is no conjugation of the phenyl group with the p pair of electrons of the O atom, the MS tensor of the $C_{ar}-O$ bond retains axial symmetry, its components are diamagnetic, and $k_L < k_T$. In anisole, in which as a consequence of $\pi_{ar}-p_o$ conjugation the $C_{sp^2}-O$ bond acquires some multiplicity, the diamagnetism is preserved for k_L, decreases for k_T, and increases for k_V. The existence of paramagnetism in the plane of the C=O double bond is therefore quite regular.

2. Magnetic Susceptibility as a Criterion of Aromaticity

The problem of aromaticity has been examined in a large number of papers on magnetochemistry, dealing with the effects of the mutual influence of atoms. Among the various indices of aromaticity which have been used, the criterion based on the MS obviously has the strongest physical foundation, since the MS tensor is determined directly by the degree of delocalisation of the π-electrons in cyclic systems. Magnetochemical studies of aromaticity have been based on the assumption that any interaction can be described quantitatively by the deviation from additivity of those properties in which this interaction is revealed. For the electric polarisability, deviations from additivity are observed not only for aromatic molecules but also for other conjugated molecules, whereas for MS, super-additive contributions for both the average values ($\Lambda = \chi_{expt}-\chi_{add}$)[141–143] and the anisotropies,[144] and also the vertical components of the tensor,[145] are characteristic mainly of aromatic compounds.

The sharp increase in the diamagnetic properties in aromatic systems compared with all other compounds has been effectively explained using the ring current model.[7,78] From the ratios of the areas of the circulation of the π-electrons (S), expressed in terms of the anisotropy of the MS

$$\sum_p S = -\gamma\,(4\pi mc^2)/e^2$$

and in terms of the geometric dimensions of the ring $\Sigma S = \pi\Sigma\bar{r}_r^2$, it is possible to determine the effective radius of circulation ($\bar{r}^2$) (for a given number of circulating π-electrons p) or the effective number of electrons involved in the circulation.[146] This method has been used to estimate the parameters $\overline{S}$ and $\bar{r}$ for a series of aromatic hydrocarbons and simple heterocyclic compounds.[147] A study of the magneto-optical properties of a number of aromatic hydrocarbons and their corresponding quinone derivatives showed that the aromatic hydrocarbons have a higher MS anisotropy than their quinones, that is the production of the quinone structure leads to a decrease in the mobility of the π-electrons: Γ(benzene)/Γ(1,4-benzoquinone) = 1.37; Γ(naphthalene)/Γ(1,4-naphthoquinone) = 1.16; Γ(anthracene)/Γ(9,10-anthraquinone) = 1.19; and Γ(phenanthrene)/Γ(9-10-phenanthraquinone) = 1.23.[148] The Cotton–Mouton effect was used for a simple estimate of the aromaticity. Thus for 1,4-dithiin, the agreement between the experimental value of ${}_mC$ and the value calculated from the additivity principle indicates that there is no electron delocalisation.[149]

The ring current model has been heavily criticised. An extreme view is that because of the additivity of the MS of aromatic hydrocarbons, the agreement between the conclusions reached from this model and the real properties of molecules is accidental.[90,150,151] This conclusion cannot be fully accepted, however, since it has not been proved that "ring currents" should not obey the rule of additivity, particularly secondary additivity. In a calculation of molecular MS, Musher[150] was forced to introduce different tensor characteristics for the C atoms involved in the formation of C–H bonds on the one hand, and the C–C bonds shared by the two condensed rings on the other. It is not excluded that this differentiation of the magnetic anisotropies includes in implicit form the differences in the change in the number of π-electrons and the areas of their circulation on going from mono- to polynuclear systems. A more correct approach is that in which the MS of an aromatic fragment is represented by two terms: a localised term (k_l) which is due to the induced currents in the individual atoms and bonds and which is calculated using an additive scheme, and a delocalised term (k_d). The latter consists of two components with opposite signs: a diamagnetic component created by the ring currents of a single aromatic π-orbital, and a paramagnetic component produced as a result of a decrease in the delocalisation.[22] For example, it follows from Ref.145 (Table 3) that in benzene the localised component describes the MS completely in the plane of the ring and to the extent of 60% in the perpendicular direction. A similar picture is observed in heterocyclic and polynuclear systems.[152–154] Thus a quantitative measure of the aromaticity (A) of any substance relative to benzene should be provided by the ratios of the perpendicular components corresponding to the anisotropies of the delocalised MS or the exaltations of the average MS for benzene and the molecule being studied (M):

$$A = [k_{\perp d}(C_6H_6)/k_{\perp d}(M)] \approx [\gamma_d(C_6H_6)/\gamma_d(M)] \approx [\bar{\Lambda}(C_6H_6)/\bar{\Lambda}(M)]\,,$$

where $k_{\perp d} = k_{\perp expt}-k_{\perp add}$, $\gamma_d = \gamma_{expt}-\gamma_{add}$, $\Lambda = \Lambda_{expt}-\Lambda_{add}$.

The replacement of a CH group in benzene by N leads to a considerable decrease in the electron delocalisation and hence in the aromaticity in the series benzene > pyridine ≃ pyridazine ≃ pyrazine > pyrimidine > S-triazine.[153] The degrees of delocalisation in pyrrole, pyrazole, and imidazole, and also their N-methyl derivatives, are similar to one another.[154] These conclusions show qualitative agreement with results obtained in a study of the Zeeman effect in isoxazole and oxazole,[152] their thio-analogues,[155] and furan;[145] the degree of delocalisation of the electrons in furan is much less than that in benzene; in oxazole and isoxazole, a further decrease in the delocalisation is observed, and the level of aromaticity of thiophene is approximately the same as that of pyrrole. An interesting feature is that cyclopentadiene also shows excess delocalisation, although to a smaller extent than in furan; this arises as a result of the hyperconjugation of the methylene group with the π-electrons of the double bonds; in fulvene, the delocalisation of the electron cloud is even smaller[145] (Table 3).

In a study of the influence of dissociation on the magnetic anisotropy of aromatic molecules by ^2H NMR in a strong field, it was established that Γ for the fluorenyl anion is greater than Γ for fluorene,[73] whereas the values of Γ for anthracene[5] and its carbacation[74] are equal.

Magnetic birefringence has been used to study the influence of the nature of the nitrogen atoms in aniline, N,N-dimethylaniline, and the corresponding anilinium and N,N,N-trimethylanilinium derivatives on the anisotropy of the MS of the phenyl group.[44,156] The anisotropy of the MS of the aromatic ring in the anilines is depressed compared with the MS of benzene, whereas in N,N-dimethylaniline the additivity is preserved; this reflects the difference in the strength of the conjugation of the lone pair of electrons of nitrogen with the

phenyl ring.[44] Protonation of aniline "restores" the magnetic anisotropy to the value characteristic of benzene. Thus the positive charge of the NH_3 group has no influence on the magneto-optical properties of the ring. The anisotropy of the N,N,N-trimethylanilinium cation decreases sharply under the influence of the excess charge.[156] This difference is due chiefly to intermolecular and not intramolecular effects;[157] in the substituent $\dot{N}(CH_3)_3$, the charge is situated chiefly on the N atom and is shielded from the hydrate layer of the solvent by the methyl groups. In the $\dot{N}H_3$ group, the excess charge is delocalised over all the N–H bonds, so that it is compensated to a considerable extent by the surrounding water molecules.

Table 3. Anisotropic magnetic susceptibilities of molecules as a criterion of aromaticity.[145]

Compound	$10^{29} k_{\parallel}$, cm^3		$10^{29} k_{\perp}$, cm^3	
	found	calculated	found	calculated
Benzene	5.80	5.55	15.71	9.87
Fulvene	5.08	5.55	11.23	9.87
Cyclopentadiene	5.53	5.61	11.21	8.39
Furan	5.30	5.20	11.73	7.80
Thiophene	6.76	6.69	15.08	9.43
Pyrrole	5.71	5.73	12.76	7.04
Durene	13.26	13.36	23.90	16.74
Resorcinol	8.17	8.39	17.14	11.81
Benzoquinone	4.15	4.78	10.80	11.05
Phthalimide	9.97	9.93	20.63	13.02
Diphenyl	10.75	10.35	30.53	18.77
Triphenyl	15.37	15.15	45.07	27.84
Dibenzyl	15.08	14.12	33.60	22.43
Stilbene	11.63	12.16	34.82	22.47
Tolane	12.41	12.86	32.94	20.68
Diphenylacetylene	15.35	14.49	34.34	21.76
Naphthalene	8.92	8.52	28.82	15.56
Anthracene	11.50	11.50	41.79	22.11
Anthraquinone	11.68	10.73	36.15	22.44
Fluorene	11.30	11.48	31.40	19.77
Acenaphthene	11.84	11.53	30.81	19.40
Pyrene	15.39	12.33	50.33	23.69

VI. MAGNETIC ANISOTROPY AND PROBLEMS OF STEREOCHEMISTRY

The systematic magnetochemical study of the spatial structure of molecules was begun comparatively recently. It is based chiefly on magneto-optical and resonance methods. Of particular interest are studies based on an analysis of the relationship between magnetic anisotropies and the chemical shifts of the ^1H and ^{13}C nuclei. The extensive information provided by this method, particularly for paramagnetic systems, the relative simplicity of the experimental procedure, and the possibility of theoretical interpretation of the results not only qualitatively but also quantitatively, led in the early nineteen-seventies to the publication of a large number of papers and to the development of an independent field, namely NMR using paramagnetic shift reagents. The method has been described in detail in many monographs, textbooks, and reviews (see for example Refs.75, 76, and 158–161), and therefore will not be discussed in the present work.

1. The Spatial Structure of Molecules and Complexes

Unlike its electric analogue, that is the Kerr effect, the Cotton–Mouton effect has been applied to conformational analysis to only a slight extent, although it should carry information on the spatial structure of molecules.[162] The molar Cotton–Mouton constants, and also the paramagnetic birefringence constants, are macroscopically additive. Moreover, the anisotropic components of ${}_mC$ and ${}_mP$ are also additive at the intramolecular level. The magnetic susceptibility of weakly magnetic substances is practically 1, so that the molecules of a solute are influenced by a magnetic field with practically the same intensity as the external field.[163] It is therefore possible to use magnetic birefringence to study the structure of molecules in the liquid condensed state. The accuracy of the results obtained using the Cotton–Mouton effect in conformation studies is such that the difference between the calculated magneto-optical constants of individual conformers is at least an order of magnitude greater than the uncertainty in their determination from the experimental data.[162]

The possibility of using the Cotton–Mouton effect in conformational analysis was first demonstrated for biphenyl (0°) and its structural analogues 2,2′-bipyridyl (25 °), 9,9′-dianthranyl (62°), 9-phenylanthracene (70°), 1-phenylnaphthalene (66°), and 1,3,5-triphenylbenzene (35°).[164] The dihedral angles φ characterising the deviations from planarity are given in brackets. In 1,3,5-triphenylbenzene and *sym*-triphenyltriazine, the angles φ are 30 ± 10° and 15 ± 15° respectively, and for tri(2-pyridinyl)-S-triazine in CCl_4, the existence of two conformers with different dihedral angles φ = 15 ± 5° has been established.[165] The measured magnetic birefringence in benzophenone and its *p*-chloro-, *p*-bromo-, *p*-methyl-, and *p*-methoxy-derivatives dissolved in CCl_4 was used to estimate the angles φ of the aromatic rings.[95] The angle of non-coplanarity of the nitrogroup in the *ortho*-position relative to the methyl group in trinitrotoluene is 50°,[93] and that in 4-nitrobiphenyl is 23°.[166] The study of individual liquid alkyl halides has confirmed that the *trans*-orientation of the C–Br bonds is preferred in methyl-substituted 1,2-dibromoethanes and cyclohexanes, and the *gauche* orientation of the C–C and C–Hal bonds is preferred in 1,3-dihalogenopropanes.[162] In the series of halogenopropanes and their methyl derivatives with the general formula $C(R^1R^2R^3)C(R^4R^5)Hal$, where Hal = Cl, Br, I, and R = H and (or) CH_3, the asymmetric *gauche* structures predominate in the pure liquids; the conformational energies of these structures are not additive, and are determined by hyperconjugative interactions $\pi[(CH_2)$ or $C(CH_3)_2] - \sigma^*(C-Hal)$.[167]

In the study of compounds containing functional groups with several axes of internal rotation, the simple application of one physical method (except diffraction methods) is insufficient. To solve a many-parameter structural problem, it is usual to employ either a combination of several methods or (and) data obtained by a single method but covering a group of compounds with the same conformation.[168] Studies of the spatial structure and conformational composition of halogen-substituted arylethanes were based on these principles.[169–172] In a complex graphical analysis of the structure of molecules,[168] new methods were proposed for determining conformations using the Cotton–Mouton effect. For this purpose, graphs of the "property–property" type are constructed: ${}_mC(C_6H_5) - {}_mC(p\text{-}X-C_6H_4)$ for a group of compounds with the same conformation,[169] and ${}_mC - {}_mK$ (${}_mK$ is the Kerr constant) for a given compound.[170] Dipole moment and ^1H NMR spectroscopic data show that 2-halogenoethylbenzenes in CCl_4 consist of equilibrium mixtures of the *trans*- and *gauche*-rotamers approximately

equally populated with respect to the ethane bond C—C. In the *gauche* form, according to data obtained using the Kerr effect, the aromatic ring shields the C—H bond. The angle of rotation of the aryl group in the *trans*-conformer was found by analysing the ${}_mC(C_6H_5CH_2CH_2Cl) - {}_mC(p\text{-}Cl-C_6H_4CH_2CH_2Cl)$ relationship.[169] The structures of 1,2-dihalogenoethylbenzenes,[171] 1,1-diphenyl-1,2-dihalogenoethanes,[172] and 1,2,2-tribromo-1-phenylethane[170] were studied similarly.

The mutual orientation of the chelate rings in molecular complexes of the lanthanides based on α,β-diketones has been studied by paramagnetic birefringence.[137,138] For the complexes of Pr and Dy with *tris*-3-trifluoroacetylcamphors, which are monomeric in $HCCl_3$ [Ln(Facam)$_3$] and dimeric in CCl_4 [Ln_2(Facam)$_6$], octahedral structures were found.[137] A structure close to octahedral was established for the adducts $Dy_2(Facam)_6.3DMF$ and $Dy(Facam)_3.2DMF$. Paramagnetic birefringence also gives information on the orientation of the molecular or ionic fragments of complexes relative to the direction of the paramagnetic anisotropy of the central ion.[47,173] In the mono-adducts of Er and Tb dipivaloylmethanates with pyridine [Ln(DPM)$_3$Py] in CCl_4, the plane of the aromatic heterocyclic ring is perpendicular to one of the principal axes of the paramagnetic susceptibility tensor.[47]

2. Orientational Effects of Solvation and Complex Formation

Magnetic birefringence and NMR spectroscopy are extremely sensitive to the effects of liquid-phase structure formation. Thus in ^1H NMR, the phenomenon of a chemical shift induced by aromatic solvents is observed; this is produced by the magnetically anisotropic continuum created by preferentially orientated aromatic molecules of the solvent arranged round the polar molecule of the solute.[174–176] New possibilities for studying intramolecular interactions influencing the alignment of molecules in liquids are being opened up by high-resolution NMR spectroscopy in strong magnetic fields.[5] In a study of the influence of the concentration of the substance and the nature of the solvent on the magnitude of the anisotropies of the MS of nitrobenzene and *m*-dinitrobenzene, a sharp decrease in the anisotropy of nitrobenzene was observed on going from the pure liquid ($\Gamma_1 = -34 \times 10^{-29}$ cm^3) to the solutions with extrapolation to infinite dilution ($_\infty\Gamma = -15 \times 10^{-29}$ cm^3).[72] In the case of benzene, a slightly different picture is observed; in $(CD_3)_2CO$, $_\infty\Gamma = -11.1 \times 10^{-29}$ cm^3, but with increase in concentration; $|\Gamma|$ begins to decrease, reaching a constant value of -9.3×10^{-29} cm^3 in a 60% solution of benzene in deuterioacetone. For naphthalene, a concentration dependence of Γ was not observed.[72] The data obtained agree with the results of magneto-optical studies;[43,62] the ratios $C_1/_\infty({}_mC)$ for benzene and nitrobenzene are of the same order of magnitude as the ratios $\Gamma_1/_\infty\Gamma$.

A quantitative approach to the estimation of the effects of liquid-phase ordering, estimated by the Cotton—Mouton method, has been proposed.[177] In the continuum model and the axially symmetrical approximation, the Cotton—Mouton constant of a solvated molecule has the form

$$ {}_mC = (2\pi N/45kT)\{2(b_\parallel - b_\perp)(k_\parallel - k_\perp) + [(b_\parallel - b_\perp)(k'_\parallel - k'_\perp) + (b'_\parallel - b'_\perp)(k_\parallel - k_\perp)]\langle(3\cos^2\theta - 1)\rangle\}, $$

where $\langle(3\cos^2\theta - 1)\rangle$ is the angular correlation factor, and b_i, k_i and b'_i, k'_i the electric and magnetic parameters of the molecules of the solute and the solvent respectively. For an individual liquid, the expression is simplified:

$$ {}_mC_l = (4\pi N/45kT)[(b_\parallel - b_\perp)(k_\parallel - k_\perp)]\{1 + (1/2)\langle\Sigma(3\cos^2\theta_j - 1)\rangle\}. $$

The corresponding solvation contribution obviously has the form:

$$ \Delta_mC = (2\pi N/45kT)(b_\parallel - b_\perp)(k_\parallel - k_\perp)\langle\Sigma(3\cos^2\theta_j - 1)\rangle. $$

Δ_mC is determined experimentally as the difference in the molar constants of the individual liquid and its dilute solutions in an inert solvent with subsequent extrapolation to infinite dilution: $-\Delta_mC = {}_mC_l - {}_\infty({}_mC_s)$. The angular correlation parameters can then be found from the relationship

$$ \Delta_mC_l/_\infty({}_mC_s) = (1/2)\langle\Sigma(3\cos^2\theta_j - 1)\rangle. $$

The numerical values of the ratios $\Delta_mC_l/_\infty({}_mC_s)$ are small, and their signs may be different; negative signs indicate the existence of chiefly ternary mutually perpendicular correlations, and positive signs indicate the existence of parallel correlations. They have been calculated for a large group of aromatic compounds.[63,64] The orientational effects of solvation are revealed most clearly in the magneto-optical anisotropy of nitrobenzene. The Cotton—Mouton constants have been obtained for nitrobenzene in 19 solvents of different character and polarity.[63] The ${}_mC$ values for this compound vary over a very wide range from $(3.3-3.4) \times 10^{-15}$ emu in dioxan, CCl_4, C_6H_6, and $HCCl_3$ to 7.5×10^{-15} emu in benzonitrile; for individual liquid nitrobenzene, ${}_mC = 6.4 \times 10^{-15}$ emu. In this case, the Cotton—Mouton constant is described by the relationship

$$ {}_mC = {}_mC_0 + A\mu\Delta k_\mu + B\mu\Delta b_\mu, $$

where Δk_μ and Δb_μ are the anisotropies of the MS and the polarisability in the direction of the molecular electric dipole moment μ. The theoretical analysis carried out indicated that a decisive role in determining the orientations round the solute molecules is played by interactions of the "solute dipole—solvent dipole" and "solute dipole—solvent quadrupole" type. A similar conclusion was reached in Refs.174—176.

In the study of the phenomena of complex formation and solvation in solutions of paramagnetic compounds, important information can be obtained by examining the effect of paramagnetic birefringence. This effect is extremely marked for complexes consisting of molecules or ions of two kinds, one of which is characterised by high anisotropy of the MS and low anisotropy of the electric polarisability, while the other has the opposite properties. For simple mixing of these species, that is in the absence of complex formation, the paramagnetic birefringence effect is small, and it is increased sharply only by the formation of associates accompanied by preferential mutual orientation of the central ion and the ligands.[173] Magneto-optical titration in CCl_4 has established the formation of an adduct of DMF with dysprosium *tris*-3-trifluoromethylacetylcamphorate with the 3:2 composition. The magnetic birefringence constant of this complex (-1300×10^{-15} emu) is approximately four orders of magnitude greater than the corresponding constant of DMF (0.17×10^{-15} emu). In an excess of DMF, the 1:2 complex is formed.[138] The formation of mono-adducts of Ln(DPM)$_3$ with pyridine in CCl_4 was confirmed similarly.[47]

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Several new fields of study have developed in molecular magnetochemistry on the basis of the study of the rotational Zeeman effect, the Cotton—Mouton effect, linear birefringence in solutions of paramagnetic substances, and the high-resolution NMR of partly

oriented molecules in strong magnetic fields. The study of the anisotropic properties of molecules gives information of a qualitatively higher level than the study of their average properties. This makes it possible to include in the range of interests of magnetochemistry a number of fundamental problems of the stereochemistry of organic and complex compounds, and intramolecular and intermolecular interactions. Among the most promising fields of application of data on magnetic anisotropy, special mention must be made of the theory of the mutual influence of atoms, and in particular the problem of aromaticity. A second field is the study of the orientational effects of association and complex formation in liquid media, the effects of structure formation appearing in pure liquids, and the structural aspects of solvation, including that in electrolyte solutions. Finally, a third field is the conformational analysis of molecules in condensed liquid media and polar solvents, and also of complex ionised species and compounds of biological importance. The progress of molecular magnetochemistry in these fields obviously depends directly on the further development and improvement of the magnetic susceptibility tensor additive scheme.

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NMR Spectroscopy of Azo Dyes

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The known NMR spectroscopy data on different types of synthetic azo and polyazo dyes, including metal complexes, are correlated. The fundamentally new opportunities in the NMR spectroscopy of ^{1}H, ^{13}C, and ^{15}N nuclei in solving problems of structural chemistry in this field of industrial chemistry are demonstrated.
The bibliography includes 124 references.

CONTENTS

I.	Introduction	941
II.	Characteristics in studying azo dyes by NMR spectroscopy	941
III.	Hydroxyazo dyes	944
IV.	Aminoazo compounds	946
V.	Labile hydroxyazo dyes. Tautomerism	947
VI.	Azo derivatives of naphtholsulphonic acids	949
VII.	Polyazo dyes	950
VIII.	Formazan dyes	951
IX.	Complex compounds of azo dyes with metal ions	952

I. INTRODUCTION

In relation to the practical application of synthetic dyes in chemistry and technology, azo compounds X−N=N−Y probably constitute the most important, diverse, and structurally ramified class of compounds.[1-5] Formazans −N=N−C(X)=N−NH− are also starting to be used actively in the chemistry of dyes.[5] While NMR spectroscopy as a powerful instrument for research into the molecular structure of compounds in solution and in the solid state is used for analysis of the structure and properties of azo dyes, the scale of its practical application falls short of the potentialities of this very same physical method and the number of unresolved problems in the chemistry of synthetic dyes. The first and until now only reviews on the NMR spectroscopy of synthetic dyes, primarily in its simplest form, appeared in the middle of the 1970's,[6,7] and they do not include the complete range of methods and wealth of opportunities which characterises the NMR spectroscopy of recent years. On the other hand, the chemistry of synthetic dyes is a forerunner of contemporary industrial chemistry and is frequently based on outdated concepts about the structure of some of its members, although many problems can be solved and have already been solved by means of NMR spectroscopy.

An attempt is made in the present work to correlate the existing NMR data on the structure and properties of azo dyes in solution and in the solid state and also on the methods of using NMR spectroscopy to resolve problems of structural chemistry in this area of chemistry.

Ideas about the actual structure of aromatic azo dyes in solution developed in spiral fashion, as so often happens, and NMR spectroscopy made a significant contribution to the solution of this problem and in a number of cases played a decisive role. By about 1970 the collection of NMR spectroscopy data obtained[8-20] (equally using other methods, see, for example one review[21]) contributed quite considerably to the understanding of the structure of these compounds in solution.[15] However, only in the last 15−17 years has the role of NMR spectroscopy in solving problems of azo dye chemistry become really significant.

The fact cannot be ignored that the structural problems of the chemistry of azo dyes and formazans are essentially inseparable from such fundamental chemical concepts as intramolecular hydrogen bonding, azo−quinone hydrazone tautomerism, internal rotation in molecules, complex formation of azo dyes with metal ions, and so forth. We have naturally taken this into account.

The aim of the present review is to show how the problems of the chemistry of synthetic azo dyes and formazans can be seen in the light of the existing information and potential applications of contemporary NMR spectroscopy. We believe that such a type of examination will be of some use to specialists working in this field of chemistry.

II. CHARACTERISTICS IN STUDYING AZO DYES BY NMR SPECTROSCOPY

(a) NMR Spectroscopy of Different Nuclei in Solution

^{1}H NMR spectroscopy has provided information about the structure of azo dyes in solution,[8-19, 22-49] including those containing a heterocyclic fragment.[34-39] In particular, information about the shielding of mobile protons in OH, NH, and SH groups, which are very frequently encountered in azo dyes, has proved productive. These and other findings provide definite information on intramolecular hydrogen bonding[8,11,18,27] and the tautomeric state[9,49] in azo dyes, on their protonation[12,13,16] and complex formation with metal ions,[28-33] and make it possible to build up initial ideas about their structure and transformations in solution.

In recent years, starting with one report,[50] a large amount of data has been obtained on the NMR spectroscopy of ^{13}C nuclei. These atoms constitute the skeleton of aromatic azo dyes and the information obtained is therefore especially useful. From the information available,[50-104] including that on compounds that do not contain functional hydroxy or amino groups,[50,81-93] it is possible to have

some idea about the electron distribution in the molecules,[50,88,89] to determine the barriers of internal rotation about the

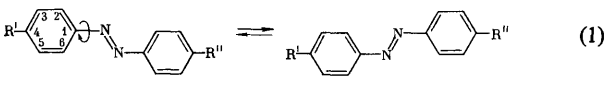


bond,[84,85] and to consider questions concerning the formation and cleavage of intramolecular hydrogen bonds in azo dyes,[59,62] the presence or absence of tautomerism in them,[70–74, 99, 101, 103, 104] and the spectral distinctions between *cis*- and *trans*-isomers.[90,91,93,100] All this information provides the necessary basis for an unequivocal interpretation of the ^{13}C NMR spectra of many types of azo dyes, including those containing heterocyclic groups.[66–69] It also provides the basis for making calculations to predict ^{13}C NMR spectra and computer knowledge of previously unstudied or newly synthesised dyes. There is also NMR information on dyes which has been obtained on ^{15}N,[93–109] ^{14}N,[20] and ^{17}O[19] nuclei; but the practical study of ^{15}N and ^{17}O nuclei at the present time is not yet as easy as it has become for ^{13}C and ^{1}H.

The NMR spectroscopy results on synthetic azo dyes are not limited to information on the shielding of their nuclei. In order to determine the structure and tautomeric state of the molecules, the results of studying various types of spin-spin coupling constant have been used, for example, mainly for ^{15}N-labelled molecules.[14,15,101, 103,106] Other techniques included in the arsenal of contemporary NMR spectroscopy have also been used—isotope effects,[94,96] temperature-dependent NMR spectra,[14,15,27] analysis of solvation effects,[62,72] two-dimensional spectroscopy,[104] and NMR titration.[57,58,64]

(b) NMR in the Solid State and Other Applications

The study of azo dyes in the solid state using high-resolution NMR spectroscopy started only in recent years.[77–80] Thus, in the first study of this type,[77] splitting of the signals from the *ortho*- and *meta*-carbon atoms was found in the solid state when the ^{13}C NMR spectra of *trans*-azobenzene and a large number of its *p,p'*-substituted derivatives (I) ($R' = R'' = H$, CH_3, OH, COOH, etc.) were studied. The overall range of differences ($\Delta\delta$) in the shielding of nuclei amounted to 13–18 p.p.m. for C(2,6) and 1.5–3 p.p.m. for C(3,5), and are thus virtually no different from what was observed in solution. The informative nature of high-resolution ^{13}C NMR spectroscopy in the solid state was demonstrated[77] when the first real example—the azo dye Disperse Orange—was studied. However, it should be emphasised that a more productive application of this branch of NMR spectroscopy is associated with solving the question concerning the unequivocal interpretation of NMR spectra, and the first steps in this direction have already been taken in the study[78] of the ^{13}C NMR spectra of Pigment Red 57:1 and for some other dyes that are azo derivatives of 2-naphthol (Pigments Red 1, 3, and 6).[80]



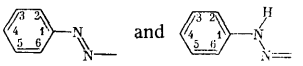
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(I)

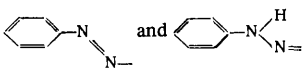
We can indicate other examples of using NMR spectroscopy that are important for the chemistry and technology of azo dyes such as analysis of the reaction of azo dyes with a substrate material,[45,46,52, 65,110] including those forming a mesomorphic phase[46] and investigation of their photo- and thermal isomerisation.[43,44,111] The aggregation of azo dye molecules in solution, and so on, has been examined.[48] All these reports undoubtedly constitute no more than the beginning of a wide range of research work which is expected to appear in the very near future, taking into account the progress in NMR spectroscopy in creating very new, extremely effective, and informative research methods.

(c) Distinguishing Features of NMR Spectroscopy in Determining the Structure of Azo Dyes in Solution

One of these is directly related to the problem concerning the effect of the azo group on shielding of ^{13}C nuclei in the aromatic ring of the diazo component of azo dyes. Thus, fairly recently the basic possibility of differences in the ^{13}C NMR spectra of the phenylazo group in two fixed and structurally distinct positions was



demonstrated.[51] This fragment was subsequently used[66,69] as a convenient diagnostic instrument in the unequivocal determination of the structure of azo dyes using NMR (in azo derivatives of 5-pyrazoline,[63,99] chromotropic acid,[55] H-acid,[61] the simplest hydroxyazo compounds used to synthesise metal-complex dyes,[59] and so forth). Moreover, this method has been successfully used for a qualitative assessment of the position of the azo–quinone hydrazone tautomeric equilibrium in azo dyes (for example, azo derivatives of 2-naphthol,[72,99] violet acid,[63] etc.). It transpired that the



groups differ markedly and clearly with respect to their shielding of carbon nuclei. When changing from a phenylazo to a phenylhydrazone group there is an upfield shift in signals from C(1), C(2), and C(4) (by ~11, 7, and 5 p.p.m. respectively). Of course, in the chemistry of synthetic azo dyes the phenyl group itself is not used so much as mono- and poly-substituted aromatic groups with the most diverse forms of substitution (depending on the problem). An appropriate correlation[109] showed that other, more commonly used aryl groups of diazo components that contain a particular substituent in the benzene ring (SO_3Na, Cl, COOH, NO_2, etc.) or a combination of certain substituents can also be used successfully for identification of the structure and conversions of azo dyes using ^{13}C NMR.

Another distinguishing feature also relates to the problem of differentiating the azo and quinone hydrazone forms of azo dyes using NMR when some hydroxy derivative of benzene, naphthalene, or anthracene acts as the azo component during their synthesis. The ^{13}C NMR signal from the carbonyl group in different types of quinoid structures is known to occur at much lower field than the signal from the $^{13}C–OH$ group in corresponding aromatic hydroxy compounds.[109] This fact was used for unequivocal identification of azo dyes in the quinone hydrazone form (examples such as arylazo derivatives of 2-naphthol,[66,67,72] chromotropic acid,[55,56] H-acid,[61] etc.) or in the azo form (examples such as derivatives of phenol,[51,52,62,64] resorcinol,[62] and 2-naphthol,[59,72] etc.).

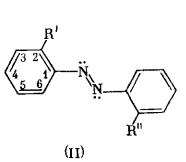
(d) Internal Rotation About the C—C Single Bond

The azophenyl fragment is known to be nonlinear in the gas phase and in the crystalline state a planar structure is the most favourable. The ^{13}C NMR spectra of *para*-substituted azobenzene (I), obtained under normal conditions, show, however, that in solution the pairs of nuclei of the *ortho*-carbon atoms C(2,6) as well as the pairs from the *meta*-carbon atoms C(3,5) are equivalent.[50,77] At low temperatures in inert solvents nonequivalence also does not occur either in the C(2,6) pair or the C(3,5) pair.[84] Thus, the available NMR data suggest a fairly rapid (relative to the time scale of NMR spectroscopy) internal rotation about the single C—N bond [reaction (1)]. This rotation is accompanied by averaging out of the shielding of these nonequivalent pairs of carbon nuclei (and, naturally, the hydrogen nuclei in ^1H NMR).

In recent years the conditions for slowing down process (1) were found when the ^{13}C NMR spectra of azobenzene derivatives in solution were studied.[84,85] The authors identified the conditions for structural modification of compounds (I) that would make it possible to increase the double-bond character of the C—N bond and slow down the internal rotation (1) accordingly. This can be achieved by the introduction of an $N(CH_2CH_3)_2$ substituent, which is often used in disperse azo dyes, at a position *para* to the azo group. As a result, in the ^{13}C NMR spectrum at a sufficiently low temperature in inert media it is possible to observe the signals from C(2) and C(6) separately ($\Delta\delta$ = 18 p.p.m.) as well as the signals from C(3) and C(5) ($\Delta\delta$ = 1.7 p.p.m.). The increase in rotation barrier about the C—N bond is determined, as the NMR data showed, not so much by steric factors as by electronic factors. In this case the electronic requirements necessary for slowing down the rotation about the C—N bond are different for the substituents acting from different sides of molecule (I). Process (1) is retarded by the introduction of an electron-donating group R′ = $N(CH_2.CH_3)_2$ on the aromatic ring side and also by the increase in electron-withdrawing capacity of the R″ group (in the series $N(CH_2.CH_3)_2$, H, NO_2) at the *para* position of the other benzene ring on the azo group side.

(e) Conformational Properties of Azophenyl Fragment

It is possible by means of NMR spectroscopy to determine unequivocally the structure of azo dyes of type (II) in solution, where groups R do not form intramolecular hydrogen bonds with a nitrogen atom.

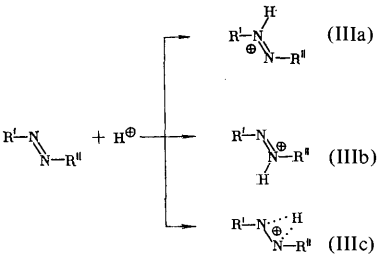


(II)

In fact, by introduction of *ortho* substituents and retardation of the internal rotation about the C—N bond, changes in shielding of the C(2) and C(6) nuclei in the ^{13}C NMR spectrum of compounds (II) take place in opposite directions. In the low-temperature splitting of the signal that corresponds to the C(2,6) nuclei in the high-temperature spectrum, the signal from the C(2) atom, which occupies the *cis* position relative to the unshared electron pair of nitrogen, is shifted downfield by about 8 p.p.m., while the signal from the C(6) atom, which occupies the *cis* position relative to the N=N bond, is shifted upfield by about 9 p.p.m.[84,85] This effect occurs in solution and at normal temperatures if the respective structural changes are made to azobenzene.[77] In particular, for 2,2′-dimethylazobenzene the C(6,6′) signal is shifted upfield by about 7.5 p.p.m. in comparison with unsubstituted azobenzene, which is clear evidence for the occurrence of only one out of three possible conformations, namely, conformation (II), R′ = R″ = CH_3. Similar results were also obtained for a wider range of compounds (II) (R′ = R″ = AlK[79]). Neither the interpretation nor the prediction of ^{13}C NMR spectra of new or previously unstudied azo dyes is possible without taking this fact into consideration.

(f) Protonation and Deprotonation of Azo Dyes

The NMR data can resolve unequivocally questions about the structural changes in aromatic and aliphatic azo dyes that occur when they are protonated in strong acid media and also deprotonated in alkaline media.



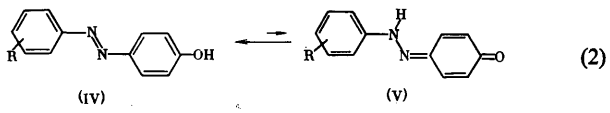
(IIIa) (IIIb) (IIIc)

In principle, the intermediates that are formed on protonation of azo dyes can have the form of (IIIa—c). NMR spectroscopy data[12,13] obtained using symmetrical model azo compounds with R′ = R″ = Ar as an example indicate that in the protonated form the aryl rings become nonequivalent (the NMR signals from indicative groups in both rings are nonequivalent). This suggests an asymmetric type of addition of the proton to the azo group. Similar results were obtained when R′ = R″ = tert-C_4H_9.[12] Thus with these results the concept of a symmetrically protonated azo structure (IIIc) can be rejected. The choice between the asymmetric structures (IIIa) and (IIIb) when R′ ≠ R″ is wholly related to the properties of the electronic effect of the R′ and R″ groups on the N=N fragment.

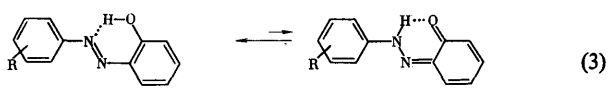
Results that are just as fundamental are given by NMR data, in particular for ^{13}C nuclei, when the consequences of deprotonation of molecules are studied (NMR titration).[64,109] The use of NMR titration to clarify the results of this chemically and industrially not infrequent situation, which occurs on alkali treatment of azo dyes, provided the answer to a number of questions concerning the structure in solution of azo derivatives of phenol,[62,64] resorcinol,[62,64] 1-naphthol,[64] and chromotropic acid.[57,58] Turning to the problem, for example, about the tautomeric form of azo dyes, ^{13}C NMR was successfully used to demonstrate, in particular, the possible occurrence of three conceivable situations during NMR titration—retention of the azo form (in phenol derivatives), its transformation from the azo to the quinone hydrazone form (in resorcinol derivatives), and its transformation from the quinone hydrazone to the azo form (in one of the 4-derivatives of 1-naphthol).[64] Even more complex situations were observed in the NMR studies of a series of azo derivatives of chromotropic acid.[57,58]

III. HYDROXYAZO DYES

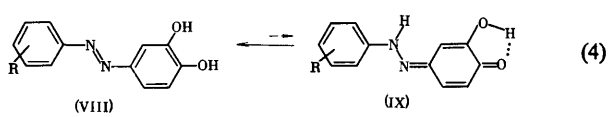
Hydroxyazo compounds constitute a considerable portion of the total number of azo dyes and include those acting as ligands in metal-complex dyes. The azo group in them is not only a chromophore but also a necessary component with an O-N type of coordination unit, because of the presence of a hydroxy substituent in the azo component.



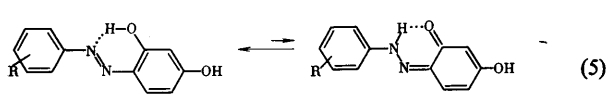
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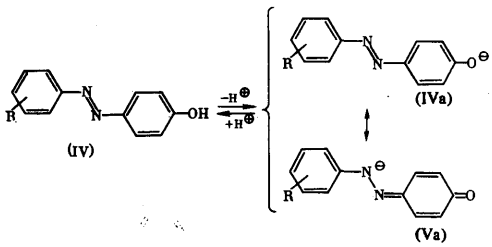
(4)



(5)

With regard to the question of the structure of hydroxyazo derivatives of benzene, which from a general hypothetical viewpoint can be represented as a mixture of products that make up tautomeric equilibria (2)–(5), there is extensive coverage on NMR in the literature. The ^{1}H,[8,14,15,17,25] ^{13}C,[59,77,99] and ^{15}N[105] NMR data suggest, however, that if diphenyl mono- and di-hydroxyazo compounds do not undergo special modification and the media conditions do not lead to complete removal of a hydroxyl proton, they only have the azo structure in solution. In other words, tautomeric equilibria (2)--(5) are shifted almost completely to the left. In fact, for each type of structure (IV), (VI), (VIII), and (X) the pattern of frequencies of ^{13}C NMR signals from the hydroxyphenyl fragment from compound to compound remains one and the same.[59] The ^{13}C NMR signal from the C–OH group, the most important in terms of identification, with allowance made for the electronic effect of the azo group in the spectra of compounds (IV), (VI), (VII), and (X) occurs in the same region as the C–OH signal of nonionised phenol: in (IV) $\delta_{C(4)}$ ~159–162.5 p.p.m.; in (VI) $\delta_{C(2)}$ ~150–154 p.p.m.; in (VIII) $\delta_{C(4)}$ ~146–147 p.p.m.; in (X) $\delta_{C(2)}$ ~153–160 p.p.m. and $\delta_{C(4)}$ ~163–166 p.p.m. These ^{13}C NMR findings can be used as a distinguishing feature in establishing the structure of the hydroxyphenylazo fragment in newly studied dyes.

In azo compounds (IV), by extrapolation from the conformational data, the proton signal from the *para*-hydroxy group in the ^{1}H NMR spectrum occurs at comparatively low field (δ_{OH} ~7.5–10 p.p.m.), and this suggests that it has a fairly acidic nature. Shielding of the hydroxy proton depends on both the properties of the substitutuent R and the properties of the medium.



In the anion form of compound (IV) the azo form (IVa) can be retained in principle, although on deprotonation it can be transformed at a given stage to the quinone hydrazone form (Va), as has been observed sometimes,[4] and these forms can be completely discrete rather than being two ways of writing the same intermediate structure. From the ^{13}C NMR data[62,64] obtained for the industrially important compounds (IV) with SO_3Na substituents at the ***meta*** position, however, it follows from the phenolate anions formed from them that in the spectra there are no fundamental differences from the corresponding anions not containing azo groups. Thus, there are no grounds for proposing the formation of the quinone hydrazone form (Va) during ionisation of azophenols.

However, the experimental data examined were obtained using the simplest examples of compounds (IV). Structural complexity of the molecules at times leads to unexpected results. An example of this is provided by the conditions identified[10,23,24,51] for shift of equilibrium (2) to the right and the existence of quinone hydrazone tautomer (V) in a series of 4-hydroxy derivatives of specifically substituted azobenzenes.

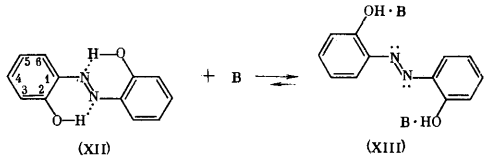
The authors[23,24] introduced electron-withdrawing substituents into the diazo component of 4-hydroxyazobenzene and electron-donating substituents into the azo component. In solutions of most of the compounds in aprotic solvents two tautomeric forms are observed separately in the ^{1}H NMR spectra—both the azo (IV) and quinone hydrazone (V) forms. Their identification was carried out by ^{1}H NMR and the ratio of tautomers was determined by integration. The ^{1}H NMR data obtained can be used to formulate the factors that determine the shift of the azo–quinone hydrazone tautomeric equilibrium (20) in either direction.

On changing from *para*- (IV) to *ortho*-hydroxy compounds (VI) the signal from the hydroxy proton is shifted downfield by 3 to 4 p.p.m. (when R = H, for example, depending on the properties of the medium and the concentration of the compound its chemical shift δ_{OH} = 12.0–12.9 p.p.m..[8,9,11,17] The magnitude of this shift is determined by the nature of the medium and the electronic and steric effects of substituents. This change in shielding of the hydroxy proton on going from (IV) to (VI) is due to the formation of a fairly strong intramolecular hydrogen bond C–O–H...N= in the respective azo structures.

Further changes in chemical shift of the hydroxy proton could be due to its intramolecular transition of NH/OH hydrogen bonding relating to the basic possibility of forming quinone hydrazone (VII). However, in reality, it hardly occurs at all in the compounds examined.

Interesting results have been obtained in studies of 2,2′-dihydroxyazobenzene (XII) using NMR. ^{1}H NMR data obtained at fairly low concentrations, which exclude the effect of aggregation, indicate that the compound has an azo structure in solution (δ_{OH} = 12.0 p.p.m. in inert media).[8,11] The same conclusion is reached when ^{13}C NMR spectroscopy is used.[59] However, when acetone-d_6

is used as the solvent instead of $CDCl_3$, in the ^{13}C NMR spectra of this compound there is a shift of the C(6) signal upfield by ~2.5 p.p.m. This fact is related to cleavage of the O—H...N intramolecular hydrogen bond in some of the molecules, in other words, there is a given shift of equilibrium (6) to the right. As a result, some of the molecules acquire a sterically more favourable conformation (XIII), in which the bulky *ortho*-substituent is aligned not in the direction of the N=N double bond but in the direction of the unshared electron pair of the nearest nitrogen atom. The average picture is recorded spectroscopically.



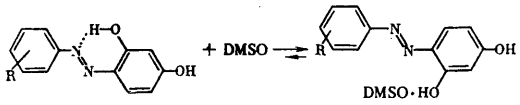
(XII) (XIII) (6)

The maximum upfield shift of C(6) that occurs assuming conformation (XIII) is more than ~8 p.p.m., and this effect occurs only in DMSO when cleavage of the intramolecular hydrogen bond occurs for all the molecules of 2,2′-dihydroxyazobenzene.[109]

In the ^{13}C NMR spectrum of 2,4-dihydroxyazobenzene—the simplest of the azo compounds (X) with a resorcinol azo component (R = H)—the pattern of frequencies of the ^{13}C signals is that expected for the azo structure and is due to the electronic effect of two hydroxy and one azo group[5] taking into account some effect from the intramolecular hydrogen bond.

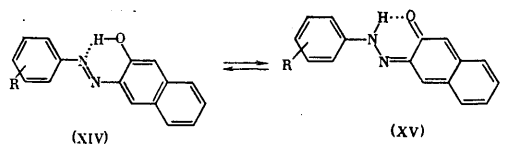
The same result is also shown by the introduction of an ^{15}N label into the compound at the N_β position.[15] The NMR signal of the proton at lower field (in this compound two hydroxy signals with δ_{OH} = 11.0 and 12.4 p.p.m. are observed), as also before introduction of the label, again proves to be a singlet over a wide temperature range although for equilibrium (5) it should have split into a doublet with the $^1J_{^{15}N-^1H}$ spin-spin coupling constant being greater the higher the content of quinone hydrazone tautomer (XI) in the mixture of (X) and (XI).

A feature of compounds of type (X) is that when acetone or alcohol is replaced by a powerful solvating medium such as DMSO, there is a marked upfield shift, which is almost the maximum possible, of the signal corresponding to C(6).[62] It is due to the replacement of an intramolecular by an intermolecular hydrogen bond with solvent, and, as a result, to the almost complete displacement of equilibrium (7) to the right and the adoption of a more favourable conformation by the compounds under these conditions:

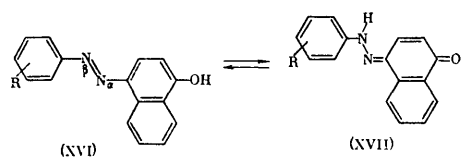


(7)

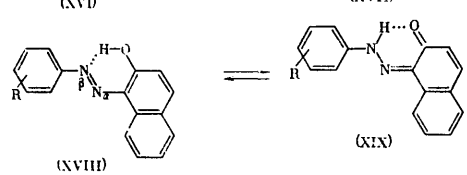
In phenyl-naphthol azo dyes, 1-naphthol or 2-naphthol act as the azo component. In principle they can participate in azo—quinone hydrazone equilibria (8)—(11). This class of compounds has been used and studied in the chemistry of azo dyes especially often.[1-5] However, in actual fact, when the equilibrium is significantly displaced in one or other direction, apparently only azo structures (XIV) and (XVI) can be identified as stable structures of this type—and then with reservations. The compounds that make up equilibrium (8) can in principle adopt both the azo form (XIV) and the quinone hydrazone form (XV). However, as it follows from the ^1H NMR data, in $CDCl_3$ they have the azo structure (XIV) (the value δ_{OH} = 12.1 p.p.m.[11] is consistent only with this type of structure). The question concerning the structure of these compounds in aqueous media remains open for the time being. Investigation of the ^1H NMR spectra of 1-benzeneazo-4-naphthol, in particular, analysis of the shape of the signal from the hydroxy proton when an ^{15}N label was introduced into the N_β position of the azo group showed[10,15] that in organic solvents this compound exists in the azo form (XVI) (R = H). ^{13}C NMR spectra obtained in nonaqueous media when R = *o*-OH are also consistent with the azo structure.[59] With regard to the possible shift of equilibrium (9) to the right in aqueous media, this question requires special consideration.



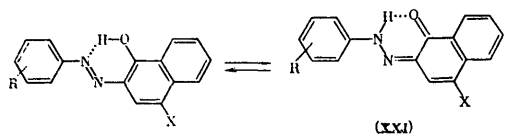
(XIV) (XV) (8)



(XVI) (XVII) (9)

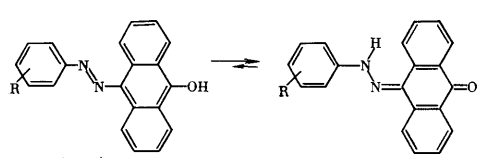


(XVIII) (XIX) (10)



(XX) (XXI) (11)

In one study[112] using ^1H NMR, the possibility of equilibrium (9) being displaced to the right (in acetone, where R = H) was discussed. However, this treatment was based on an analysis on the signal observed in solution with δ_{OH} = 3.59 p.p.m. (corresponding to an impurity, as has been revealed[70]) and consequently on an incorrect assignment of the main signal with δ_{OH} = 10.2 p.p.m. to the quinone hydrazone form (XVII), although in reality it belonged to the azo form of this compound (XVI).

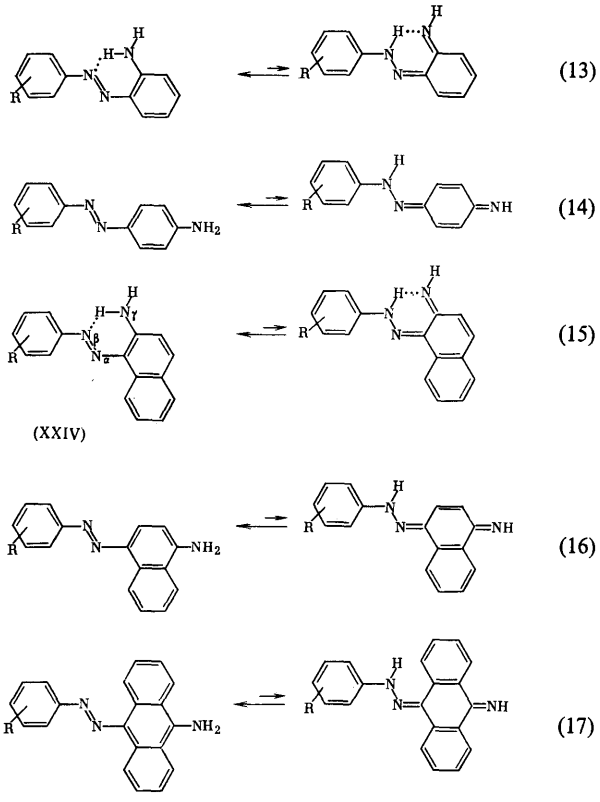


(XXII) (XXIII) (12)

The last example from the number of basically distinct, stable aromatic hydroxyazo systems is 9,10-anthraquinone phenylhydrazone. According to ^1H [15] and ^{14}N [20] NMR data, this compound exists in the quinone hydrazone form (XXIII) (equilibrium (12) displaced to the right). Conformation of this is provided by the appearance of a $^{15}N-^1H$ spin-spin interaction in the ^1H NMR spectrum with a coupling constant that is independent of the temperature.

IV. AMINOAZO COMPOUNDS

The conditions for formation of an iminoquinone hydrazone structure among aromatic aminoazo dyes is less favourable compared to hydroxyazo dyes as a result of the lower acidity of the NH proton compared to the OH proton and as a result of the differences in geometry for configuration of the proton in a hydrogen bond. Positive indications of the azo structure in aminoazo dyes are given by both ^1H [27,41] and ^{13}C [60,70,101] NMR spectroscopy data.



(13)

(14)

(15)

(XXIV)

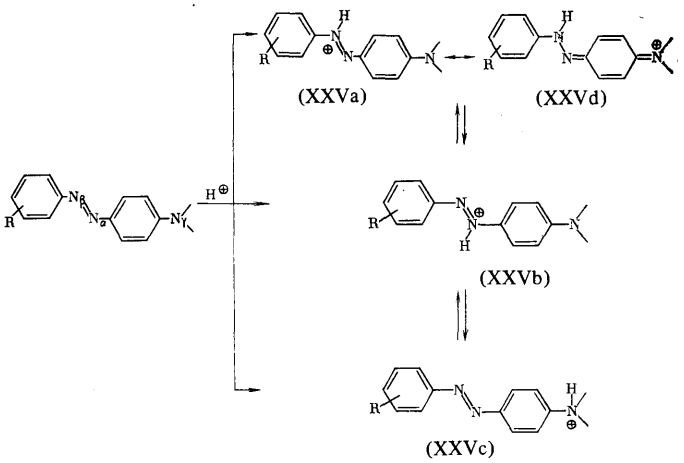
(16)

(17)

According to ^1H NMR data,[27] in the dye Fat Yellow AB (XXIV) (R = H) and in azo dyes (XXIV) in general it is the shielding of the NH proton that participates in intramolecular hydrogen bonding that suggests an azo structure, namely a complete displacement of the hypothetical equilibrium (15) to the left. At fairly low temperatures the signals from the protons of the amino group in (XXIV) are split; the proton contained in the N–H...N hydrogen bond has a shift δ_{NH} = 10–10.2 p.p.m., while the free proton has δ_{NH} = 5–5.3 p.p.m. On the other hand, in iminoquinone hydrazone structures the NH proton is shifted to lower field (δ_{NH} = 14 to 16 p.p.m.). The fact that both NH protons in these compounds are located precisely on N_γ was confirmed[27] by the introduction of an isotopic label N_γ = ^{15}N. In this case both the NH_2 protons are split by the ^{15}N nucleus with approximately the same constant. Accordingly, introduction of a ^{15}N isotope to replace N_β did not lead to splitting of the NH proton.

The ^{13}C NMR data[60,70,101] gave the same results. As was demonstrated in one study,[101] the azo structure actually occurs not only in substituted azobenzenes, where equilibria (13) and (14) could be assumed, but also in more complex compounds in which the amino group is joined to naphthalene or anthracene aromatic systems [hypothetical equilibria (15)–(17)]. In the ^{13}C NMR spectrum of the phenylazo derivative of aminoanthracene, for example, as in a number of related compounds, the chemical shifts of the different nuclei in the characteristic phenylazo group are clearly consistent with the azo structure of the $C_6H_5-N=N-$ fragment, namely, with the complete displacement of equilibrium (17) to the left. It is significant that the spectrum of the naphthylamine fragment of (XXIV) is the same regardless of the properties of the substituent R in the phenylazo group.[60,70,101] In this case the frequency pattern of the ^{13}C NMR signals from the naphthylamine fragment is consistent with its azo structure and is not satisfactorily interpreted on the basis of the iminoquinone hydrazone structure. The lack of dependence of the shielding of the NH proton participating in hydrogen bonding on the properties of substituent R was also observed in the ^1H NMR spectra of these compounds.[27]

Let us examine the NMR spectroscopy data on *para*-aminoazobenzene derivatives. Introduction of an amino group leads to a situation where in *para*-aminoazobenzene itself (Disperse Diazo Claret) and in dyes of this type in general (Fat Soluble Yellow 2G, Methyl Organe, etc.) that have three basic centres N_α, N_β, and N_γ, three monoprotonated structures (XXVa–c) that differ according to the site of proton attack, including two isomers (XXVa) and (XXVb) that are asymmetrically protonated on the azo group, can in principle occur:



(XXVa) (XXVd)

(XXVb)

(XXVc)

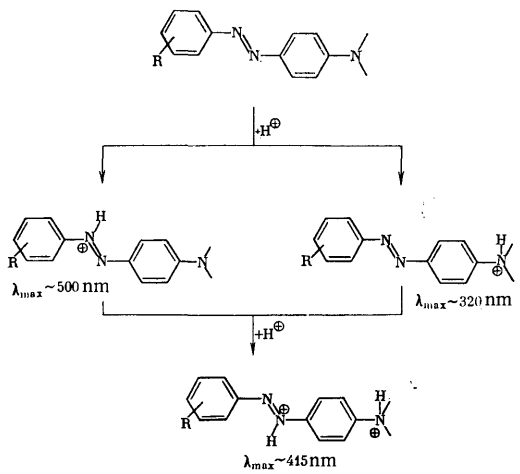
There is an interesting debate[1,2,21] over the interpretation of the spectroscopic data on the protonation of aromatic aminoazo dyes. It is based on the suggestion of the possible occurrence in these compounds of tautomerism of the form:



There has also been a discussion on the question concerning the addition site of a proton to the azonium cation—either to the α- or β-position.

These problems can be resolved almost completely using the NMR data. In weakly acid media these derivatives form one or both monocations—ammonium salt (XXVc) and one of the azonium salts. Making use of the arguments of NMR spectroscopy we can, in addition to ^1H NMR studies,[12,13,16] also indicate other works,[88,95]

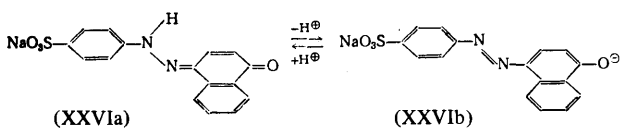
where a sample of Disperse Diazo Claret enriched with ^{15}N was analysed on its ^{13}C and ^{15}N nuclei. The authors showed that in a weakly acid medium the proton adds on either to N_γ or to N_β. The first isomer predominates in solution, while in the second isomer the distribution of electron density corresponds precisely to azonium structure (XXVa) and not to mesomeric structure (XXVd). Thus, on the basis of a direct NMR experiment, two questions are resolved—the site of addition of the proton to the azo group (N_α or N_β), namely, identification of cation (XXVa) or (XXVb), and the structure of the azonium cation formed. Addition of the proton to N_β is evidently due to the orienting effect of the *para*-amino group. In strong acid media there is a structural transformation in the dication formed, and the second proton is found to be added not to N_β but to N_α. Taking into account these results, protonation of Disperse Diazo Claret and related azo dyes can be represented as follows:



V. LABILE HYDROXYAZO COMPOUNDS. TAUTOMERISM.

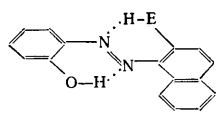
From the four phenylnaphthol hydroxyazo systems (8)–(11), usually a given limiting tautomeric form does not occur in the two depicted in equilibria (10) and (11) but there is an azo–quinone hydrazone tautomeric equilibrium. Conditions can be selected when tautomeric system (9) also becomes labile; NMR data relating to the preferred formation of the azo form for this was given above.

When Orange I (structure (XVI)/(XVII), R = *p*-SO_3Na) was studied using ^{13}C NMR, it was found[65] that the chemical shift of the C(4) nucleus was 186.3 p.p.m. (probably in D_2O). Although the authors[65] interpreted the results in favour of the azo structure (XVI), the magnitude of the shielding of C(4) objectively indicates the quinone hydrazone structure (XVII), namely, the complete displacement of equilibrium (9) to the right. A subsequent study of this dye using NMR showed[64] that the change of colour it undergoes in an alkaline medium is due to conversion (18), which occurs by deprotonation, namely, transformation of neutral quinone hydrazone form (XXVIa) to the ionised azo form (XXVIb).

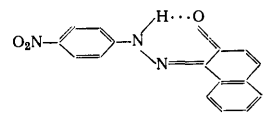


(XXVIa) yellow (XXVIb) red (18)

Arylazo derivatives of 2-naphthol constitute a large group of azo dyes (Fat Soluble Orange, Fat Soluble Orange 2K, Pigment Red G, Fat Soluble Dark Red, Chrome Violet K, Acid Orange G, Pigment Scarlet, etc.) that are not without significance in dye chemistry and are very interesting from the methodical viewpoint. It is not possible to assign a definite structure to these azo dyes but they should be regarded as forming azo–quinone hydrazone equilibrium (10). This equilibrium has been studied by NMR in relatively greater detail than the others—under different conditions and using various techniques of NMR spectroscopy.[8,10,14,15,19,20,49,59,70–74,80,99,106] Thus, when 1-benzeneazo-2-naphthol (Fat Soluble Orange dye; structure (XVIII), R = H) was studied, it was found[8] that the signal from the hydroxy proton was shifted downfield by ~3 p.p.m. relative to *ortho*-hydroxyazobenzene and 2,2′-dihydroxyazobenzene. Although an explanation for this effect was given in terms of azo structure (XVIII) (assuming that a stronger C–O–H...N hydrogen bond is formed in (XVIII) than in *ortho*-hydroxyazobenzenes), such an explanation could not be the only one since in the absence of any substantial structural changes in comparable hydroxyazo compounds that include the same type of intramolecular hydrogen bonding the magnitudes of the effect found[8] are too high. An alternative conclusion followed from ^{17}O NMR findings,[19] which indicated a certain double-bond character of the C–O bond, namely, some displacement of equilibrium (10) to the right. In other words, the downfield shift of the signal from the OH proton that occurs in compounds of type (XVIII) is due not so much to the increase in strength of the COH...N bond as to its change of form (C–O–H...N → C=O...H–N), namely to the development of azo–quinone hydrazone tautomerism (10). In subsequent NMR studies[10,14,15,20,49,59,70–74,80,99,106] the authors started precisely from this point and studied the dependence of the position of equilibrium in tautomeric system (10) on different factors such as the temperature of the solvent, type of medium, and changes in structure of the azo dye.



(XXVII) a) E = O, b) E = NH



(XXVIII)

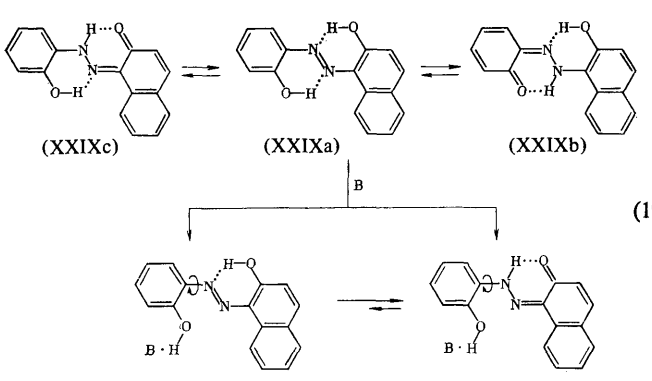
In particular, examples of the limiting tautomeric forms of these compounds—(XXVII) and (XXVIII)—were found, according to the ^{13}C NMR data.[59,70,109] In compounds (XXVII), studied in the polar but nonsolvating medium of chloroform, the experimental chemical shifts of the C(2) and C(4) nuclei ($\delta_{C(2)}$ ~153–155.8 p.p.m.; $\delta_{C(4)}$ ~133–136 p.p.m.) are similar to those calculated for a proposed azo structure. Here equilibrium (10) is displaced to the left and stabilisation of the azo form is achieved by two O–H...N hydrogen bonds that are similar in structure in (XXVIIa) or by the combination of different hydrogen bonds N–H...N and O–H...N in (XXVIIb). The dye Pigment Red G, on the other hand, has the quinone hydrazone structure (XXVIII), as is indicated by the value of the chemical shift $\delta_{C(2)}$ ~180 p.p.m., which is characteristic of the ketone group in the quinonoid ring, as well as by the significant change in chemical shift of C(4) ($\delta_{C(4)}$ = 143.5 p.p.m.). For this dye equilibrium (10) is displaced to the right.

Several NMR methods have been suggested for qualitative and quantitative determination of the position of the tautomeric equilibrium in system (10): a) from the change in proton chemical shift δ_{OH},[10,20] and also $\delta_{H(3)}$ and $\delta_{H(8)}$;[70] b) from the change in δ_{14_N}

chemical shift of the N_β atom, which participates in the hydrogen bond (since the NMR signal in this case is measured under conditions of $^{14}N-\{^1H\}$ double resonance, these determinations are evidence for a six-membered ring of the hydrogen bond with N_β, as is depicted in (XIX), and not a five-membered ring with N_α;[20] c) from the changes in chemical shift of $^{15}N_\beta$ and $^{15}N_\alpha$ and also the direct spin-spin coupling constants $^1J_{^{15}N-^1H}$ and $^1J_{^{15}N-^{15}N}$ (due to the low content of natural ^{15}N isotope, a ^{15}N isotopic label was introduced for the measurements in these studies;[14,15,106] d) from the changes in chemical shifts of ^{13}C nuclei of specific atoms in the system, those most sensitive to its changes of state.[71,72,99] All these methods require a knowledge of the measured radiospectroscopic parameter for the limiting positions of the tautomeric system—for the pure azo form and for the definitely proved quinone hydrazone form—and assume a linear dependence of the measured parameter on the content of tautomers in the mixture.

Results[71,72,99] indicate that ^{13}C NMR spectroscopy is particularly successful in determining the ratio of the individual tautomers (XVIII) and (XIX) and the equilibrium constant of (10). One modification of this method is suitable for studying the temperature dependence of the position of tautomeric equilibrium [using the data on the change in chemical shifts of some types of ^{13}C nuclei of the unsubstituted benzene ring in 2-benzeneazo-2-naphthol (Fat Soluble Orange) or, generally, a substituted but fixed phenyl ring and a naphthol residue]. The effect of structural factors on the position of equilibrium (10) is more convenient to study from the shifts in the structurally invariable part of the molecule, namely, from the changes in shifts of the C(2), C(3), and C(4) nuclei of the naphthalene ring in relation to the substituents in the benzene ring, since the variation in shielding of ^{13}C nuclei in these positions is more sensitive to structural changes in the molecules.[71,72] Structures (XXVIIa) (studied in chloroform) and (XXVIII) can be used as reference compounds.

Dihydroxyazo compound (XXIX) (Eriochrome Violet C), which is one of a series of compounds for which equilibrium (10) is possible and one of the main types of dye,[1-5] deserves special consideration. According to the ^{13}C NMR data,[59] this compound in chloroform has only the azo structure (XXIXa) and there were no indications that the quinone hydrazone forms (XXIXc) and (XXIXb) existed under these conditions. Thus, equilibrium (19) does not actually occur in nonsolvating media.

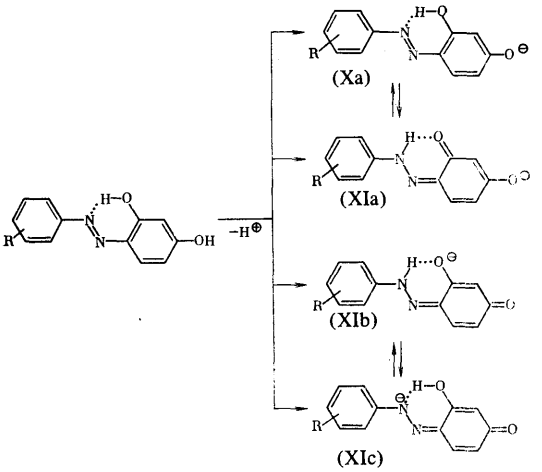


(19)

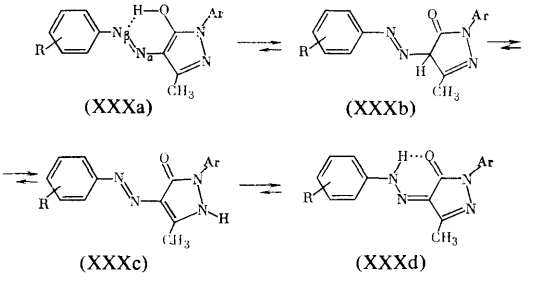
The displacement of the azo—quinone hydrazone equilibrium for compound (XXIX) towards azo structure (XXIXa) is apparently due to the formation of two O—H...N hydrogen bonds of similar structure. In one study[72] an attempt was made to find a solvation method (as opposed to a structural method) for conversion of the fixed tautomeric azo form to the corresponding tautomeric equilibrium.

It transpired that when chloroform was replaced by acetone and even more so by DMSO, the ^{13}C NMR spectrum of the compound changed considerably. Instead of the fixed tautomer (XXIXa), an equilibrium such as (19) occurs in solvating media. Strongly solvating media B that have basic properties promote the cleavage of one of the two hydrogen bonds (the weaker one), as a result of which in the compound with the remaining hydrogen bond the stabilisation conditions are virtually the same as those in other compounds with a substituent at the 2-position that does not form a hydrogen bond with the N=N group. Consequently, most of the molecules undergo a change in the type of hydrogen bond (N...H—O—C → N—H...O=C).

As has already been stated, resorcinol azo dyes in the neutral form have azo structure (X). However, a tautomeric conversion to the quinone hydrazone form was found in alkaline media by elimination of the primary, more acidic proton of the *para*-hydroxy group that does not participate in hydrogen bonding.[62,64]



The NMR spectroscopy data for azo dyes of type (X) (Sudan G, R = H; Azo Violet, R = *p*-NO_2; Resorcinol Yellow, R = SO_3Na) indicate that a quinonoid carbonyl group with chemical shift $\delta_{^{13}C-O}$ = 185—186 p.p.m. is formed in an alkaline medium. Thus, azo form (Xa) can be excluded as the monoanion state of resorcinol azo derivatives; in an alkaline medium they have one of the quinone hydrazone structures (XIa—c). From NMR titration curve graphs that were obtained[64] for compound (X), where R = *m*-SO_3Na, it was possible to make a more definite choice in favour of *para*-quinoid structure (XIb).

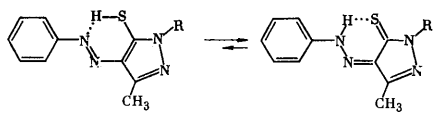


(20)

For dyes with a pyrazolone azo component, azo structure (XXXa) is to be expected from a traditional viewpoint.[5] An alternative approach with regard to possible tautomerism requires not just two

but four tautomeric forms (XXXa–d) to be considered for equilibrium (20). The "hybrid" forms (XXXb) and (XXXc), however, were ruled out many years ago by the first NMR studies (in the ^1H NMR spectrum of certain arylazo derivatives of 1-phenyl-3-methyl-5-pyrazolone, signals due to CH and NH protons not involved in hydrogen bonding were absent).[34-37] From the value of the chemical shift of the proton participating in NH/OH hydrogen bonding in nonsolvating media (δ_H = 13.5–13.8 p.p.m.[34,36]) and the changes in the ^1H NMR spectrum of the compound when it underwent N- and O-methylation it was possible to conclude further that out of the two more traditional tautomeric forms (XXXa) and (XXXd) keto form (XXXd) actually occurs in arylazo derivatives of 5-pyrazolone.[10,34,36] Confirmation of this was obtained[15,106] by introduction of a ^{15}N label into the β-position. In the ^1H and ^{15}N NMR spectra in chloroform there was a doublet which suggested the existence of a $^{15}N-^1H$ bond as part of the hydrazone form (XXXd).

The ^{13}C NMR data[54,63,99] are consistent with these results. Without dependence on the properties of the substituent in the aromatic diazo component and in the N-aryl azo component, the ^{13}C NMR spectra of the pyrazolone skeleton are only consistent with quinone hydrazone form (XXXd) for all the azo dyes based on 5-pyrazolone that have been studied, including the simplest, Fat Soluble Yellow 3 (R = H and Ar = C_6H_5) and more complex ones such as Acid Yellow Fast (R = H and Ar = p-$NaO_3SC_6H_4$), etc. These results can also be used to analyse the ^{13}C NMR spectra of other dyes of this class that have not previously been studied or have recently been synthesised.



(21)

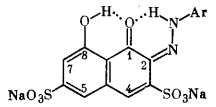
(XXXIa) (XXXIb)

The results are similar for azo derivatives of 5-thiopyrazolone. It follows from the ^1H NMR data[47] that the hydrogen atom involved in NH/SH hydrogen bonding occurs at very low field (δ_H = 16.68 p.p.m. when R = C_6H_5 and 16.20 p.p.m. when R = CH_3). This result together with the ^{13}C NMR data[54] clearly suggest that these compounds have quinone hydrazone structure (XXXIb) (in other words, the hypothetical equilibrium (21) is displaced to the right), although the azo structure (XXXIa) was preferred by the authors of one study.[47]

VI. AZO DERIVATIVES OF NAPHTHOLSULPHONIC ACIDS

Azo derivatives of 1-naphthol- and 2-naphthol-sulphonic acids (Nevile and Winther's acid, Schaeffer's acid, G- and H-acids, etc.) and also 1-8-dihydroxynaphthalene-3,6-disulphonic acid (chromotropic acid) and 1-hydroxy-8-aminonaphthalene-3,6-disulphonic acid (H-acid)[1-5] occupy a position of important practical significance. Study of them by means of ^1H and ^{13}C NMR spectroscopy is essentially only beginning,[52,53,55-58,61,63-65,104] and the ^{13}C NMR data obtained for the initial naphtholsulphonic acids[113-115] is proving to be effective for this.

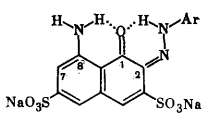
In the past it happened that in the studies devoted to dyes such as monoazo derivatives of chromotropic acid, the azo form of these compounds was usually a fundamentally accepted principle, and this transition has been preserved until recently. The structure and properties of both types of monoazo-substituted H-acid obtained under alkaline and acidic conditions and of monoazo-substituted Schaeffer's acid, G-acid, Violet acid, and others have also only been considered in terms of the azo structure.[5] The ^{13}C NMR spectroscopy data obtained for monoazo-substituted chromotropic and H-acids,[55-58,61,104] and equally for other compounds of this particular type,[52,53,63,104] necessitate a re-examination of these views.



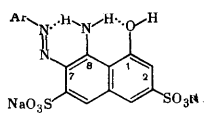
(XXXII)

Thus, it follows from the results obtained[55-58] that dyes of the form of monosubstituted derivatives of chromotropic acid have one and the same quinone hydrazone structure (XXXII). This applies not only to the simplest dye in the series—Chromotrope 2R (Ar = C_6H_5)—but also to any of the more complex structures—Victoria Violet BS, Acid Blue 3, Chromotrope 6B, etc. The main spectral feature of all the dyes is the presence of a signal with chemical shift 179–182 p.p.m. corresponding to C(1) in the naphthalene region of their ^{13}C NMR spectra. Signals from the carbonyl group of quinonoid compounds (in 1,2-naphthoquinone, for example, $\delta_{C(1)}$ = 180.9 p.p.m.[109]) are known to occur in this region of the spectrum.

Thus, in none of the dyes does the corresponding tautomeric equilibrium actually occur since it is displaced towards the quinone hydrazone form (XXXII). In this case the keto group of the dyes participates in the formation of two intramolecular hydrogen bonds to give six-membered rings—a particularly strong keto–enol O–H...O=C bond and an additional keto–amine O...H–N bond. For the alternative azo structure, the intramolecular hydrogen bond in which the C(1)–OH naphthol group would be expected to participate is noticeably weaker.



(XXXIII)

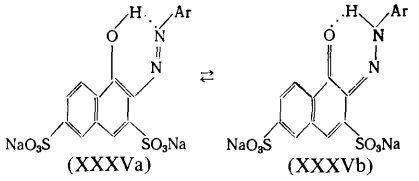


(XXXIV)

In monosubstituted derivatives of H-acid obtained in alkaline media (that is, synthesised under conditions where the site of addition of the arylazo group can only be the C(2) atom of the initial H-acid), for all the dyes investigated, either without (Acid Strong Fuchsin 2B) or containing a given substituent in the side chain, there is a ^{13}C NMR signal in the region 181–182 p.p.m.[61,104] This result is consistent only with the quinone hydrazone structure (XXXIII) and does not support the traditionally held view. For monosubstituted derivatives of H-acid that are synthesised under acid conditions where there is attack on the C(7) atom, it follows from the NMR data[61] that in this case the dyes formed exist in solution only in the azo form (XXXIV) similar to that observed in other azo derivatives of naphthylamine.

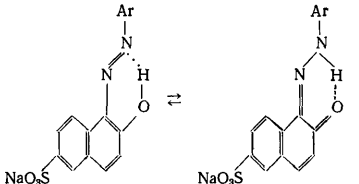
In one study[63] ^{13}C NMR data are reported on dyes of type (XXXV) (monosubstituted derivatives of violet acid), which do not contain a functional group at C(8) to participate in the formation of an intramolecular hydrogen bond. As a result, tautomers (XXXVa) and (XXXVb) exist at the same time in solution, although equilibrium (22) is displaced to the right to a considerable degree. Thus, while in monoazo derivatives of chromotropic and H-acids (XXXII) and (XXXIII)/(XXXIV) the respective tautomeric equilibria are only

theoretically possible, in derivatives of Violet acid (XXXV) the absence of additional six-membered rings involving keto–enol O–H...O=C or keto–amine N–H...O=C hydrogen bonding makes tautomeric equilibrium (22) quite real, observable, and it can be displaced by the effect of particular factors, structural or solvation.



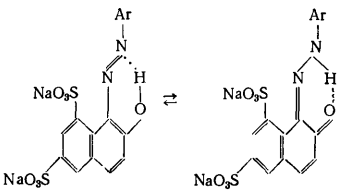
(XXXVa) (XXXVb) (22)

The ^{13}C NMR data which relates to several monoazo derivatives of Schaeffer's acid that are substituted in the aryl ring (Acid Brilliant Orange G) clearly suggest that azo–quinone hydrazone equilibrium (23) occurs in these dyes.[52,53] In this hypothesis the substantial differences in the experimental ^{13}C NMR chemical shifts from those calculated by the authors[52,53] for the traditional hypothesis of only the azo structure (XXXVIa) can readily be explained. The use of the method of calculation proposed in recent studies[63,72] in assessing the ^{13}C NMR data[52,53] leads to the conclusion that in system (23) when Ar = *m*-$NaO_3SC_6H_4$ the compound occurs to about 90% in the quinone hydrazone form (XXXVIb).

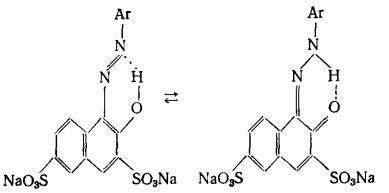


(XXXVIa) (XXXVIb) (23)

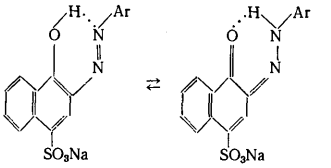
In some studies[52,53,104] ^{13}C NMR was used for the first time to study individual examples of dyes that actually (if the chemical shifts of the $\delta_{13_{CO}}$ nuclei obtained by the authors are analysed objectively) exist as equilibrium mixtures (23)–(26) as well as a number of other systems. Since the assessment of the ^{13}C NMR data in two studies[52,53] was made, in contrast to the other study,[104] from the traditional standpoint of the azo structure without including ideas about the possible occurrence of azo–quinone hydrazone tautomerism in these compounds, a reinterpretation of these findings and a possible reassignment of some signals is inevitable.



(24)



(25)

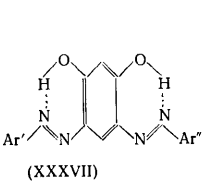


(26)

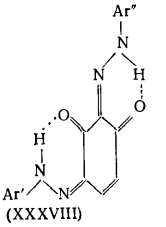
It is well known that azo-substituted derivatives of chromotropic acid as well as many other dyes are used over a very wide region of variation in the acidic and basic properties of the medium. In this connection, studies on the changes in the ^{13}C NMR spectra of azo dyes (XXXII) with the pH of the medium[57,58] are important. Although this aspect of the problem can include several different situations, there are two that are the most important. The first case occurs when there is a proton-donor group R (R = COOH, OH, AsO_3H_2, etc.) at the *ortho* position of Ar. In this case a corresponding structural complexity is possible in the compounds as a result of the formation of additional intramolecular hydrogen bonds. The second case occurs when the *o*-R group in Ar is a fairly "inert" group in relation to the formation of an additional hydrogen bond (R = Cl, CH_3, etc.). The first case has been examined[57] for R = AsO_3H_2. It transpired that in aqueous media the region for the compound existing in the azo form (more precisely, as the corresponding azo–quinone hydrazone equilibrium) is quite narrow—only in a weakly alkaline medium when the hydroxyl proton at C(8) still remains sufficiently strongly bonded to the oxygen atom. The second case was analysed[58] using a series of compounds with an "inert" *ortho*-group R. Here the changes in chemical shifts of the C(5)–C(9) nuclei, situated near the C(8)–OH hydroxy group, are in qualitative agreement with the successive change in pH observed in 1-naphthol and phenol up to complete removal of the hydroxy proton. In this case both tautomeric forms coexist in alkaline media to an approximately equal extent.

VII. POLYAZO DYES

Bis- and poly-azo aromatic derivatives are among the most important compounds industrially, but their previous study by means of NMR spectroscopy has been particularly brief[9,15,18,53,56,61,109]



(XXXVII)

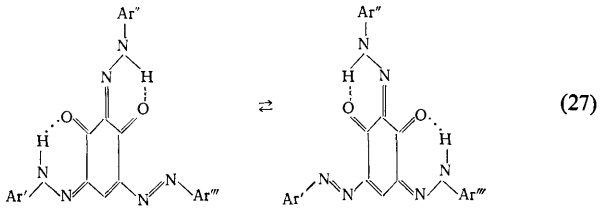


(XXXVIII)

It follows from the respective ^1H NMR data[18] that both *bis*-azo compounds synthesised from the monofunctional azo component phenol, have the azo structure in solution, as do the monoazo compounds.

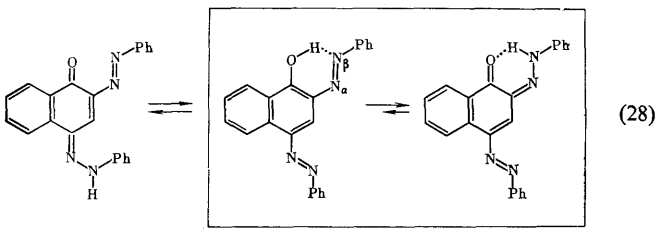
The NMR data on *bis*-azo derivatives of difunctional azo components such as resorcinol reveal a more complex picture. According to ^1H[9,18] and ^{13}C NMR[109] data, out of two structures the 4,6-isomer has the traditional *bis*-azo form (XXXVII). On the other hand, the 2,4-isomer occurs in a quite unexpected *bis*-quinone hydrazone form (XXXVIII). The shielding of the protons that participate in the two slightly nonequivalent NH...O hydrogen bonds does not leave open the possibility in the latter compound (δ_{NH} = 15.7 and

16.6 p.p.m. in $CDCl_3$ [9] and in DMSO;[18] $Ar' = Ar'' = C_6H_5$) of proposing any small amount of the corresponding mixed azo–quinone hydrazone forms. The ^{13}C NMR spectroscopic data is completely consistent with these results.[109] The conclusion about the structure of the 2,4- and 4,6-isomers as (XXXVIII) and (XXXVII) is consequently extremely important for understanding the structure in solution of dyes such as Acid Leather Brown 3K (XXXVIII), Acid Leather Light Brown (XXXVII), etc.



(27)

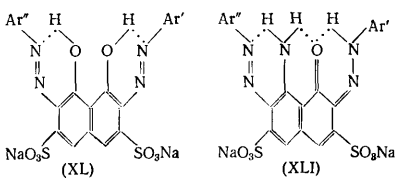
The *bis*-quinone hydrazone form of the *tris*-azo derivative of resorcinol ($Ar' = Ar'' = Ar''' = C_6H_5$) is sufficiently stable only at fairly low temperatures.[109] With an increase in temperature changes occur in the ^1H and ^{13}C NMR spectra that correspond to interconversion (27) of two *bis*-quinone hydrazone forms (when $Ar' = Ar'' = C_6H_5$ are equivalent). These findings are important for understanding the properties of the dye Acid Leather Brown K.



(28)

(XXXIXb) (XXXIXa) (XXXIXc)

NMR data that relates to the *bis*-azo derivative of 1-naphthol [system (11), R = H, X = N=N–C_6H_5] have been reported.[15,103] In this dye, which traditionally could have been represented as (XXXIXa), there are two possibilities for formation of a quinone hydrazone form—(XXXIXb) and (XXXIXc). By introducing a $^{15}N_\beta$ isotope label the authors of one study[15] ruled out the 1,4-quinone hydrazone form (XXXIXb). A positive indication of the 1,2-quinone hydrazone form (XXXIXc) is given not only by the doublet splitting of the labile NH proton in the ^1H NMR spectrum of the labelled compound but also by the magnitude of shielding of this proton (δ_{NH} = 15–16 p.p.m.). From the change in the value of the $^1J_{^{15}N-^1H}$ constant as the temperature was decreased it was possible to establish that equilibrium (28) is displaced almost completely to the right under these conditions.

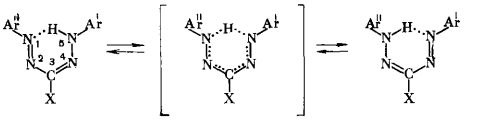


(XL) (XLI)

When we consider the 2,7-*bis*-azo derivatives of chromotropic acid and also H-acid, we can observe a basic difference in them. According to the ^{13}C NMR data,[56] the derivatives of chromotropic acid have the *bis*-azo structure (XL) in solution, which is quite distinct from quinone hydrazone structure (XXXII) that is typical for the corresponding monazo derivatives. On the other hand, the NMR spectroscopy data[61] for *bis*-azo derivatives of H-acid are consistent with structure (XLI), combining, as it were, both types of monoazo derivative obtained in alkaline and acid media [quinone hydrazone structure (XXXIII) and azo structure (XXXIV) respectively]. This applies, for example, to some well-known dyes such as Acid Blue Black ($Ar' = C_6H_5$, $Ar'' = p\text{-}O_2NC_6H_4$) and Acilan Dark Green B ($Ar' = C_6H_5$, $Ar'' = p\text{-}H_2NC_6H_4$).

VIII. FORMAZAN DYES

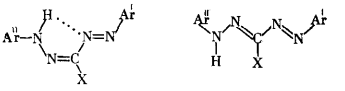
Formazan dyes have already been fairly widely accepted for solving practical problems.[5] They exist in two forms, "red" and "yellow", depending on the properties of the substituent X at the *meso*-carbon atom. There has until now been comparatively little NMR data[116–124] relating to formazans and their complexes with metal ions. In solution the "red" 3-X-1,5-diarylformazans (X = NO_2, Ar, and certain other groups that prevent the compounds being classified as dithizone derivatives, that is, when X ≠ SR) exist as equilibrium mixtures (29) of two cyclic *syn-s-cis* forms (XLIIa) and (XLIIc) with N(1)...H–N(5) and N(1)–H...N(5) intramolecular hydrogen bonds. When metal-complex dyes are formed the metal ion is introduced into the centre of the formazyl group with displacement of the hydrogen atom.



(29)

(XLIIa) (XLIIb) (XLIIc)

In 1,5-diarylformazans the N...H–N hydrogen bond is fairly strong (energetically favourable six-membered ring) but not so much as to exclude when there are certain forms of X (for example, when X = Cl, CH_3, etc.) the possibility of these compounds existing in solution in the "yellow" form, where the formazyl group acquires the *syn-s-trans* configuration (XLIII) with a weaker hydrogen bond as part of a five-membered ring or even the *anti-s-trans* structure (XLIV) completely without intramolecular hydrogen bonds (stabilised by intermolecular hydrogen bonding).



(XLIII) (XLIV)

It follows from ^1H [116–121] and ^{13}C [122–124] NMR data on compounds in which group X does not participate in the formation of strong hydrogen bonds that in relation to the NMR parameters these compounds can be separated into two groups that are chemically distinct. In the "red" formazans the signals from the NH protons occur in a region characteristic for compounds with strong intramolecular hydrogen bonds [δ_{NH} = 13.7–15.7 p.p.m. in $CDCl_3$);[117,119,121] structures (XLIIa) and (XLIIc)], and their chemical shift is only slightly dependent on the properties of the medium.[118] In the "yellow" formazans the chemical shift of the NH protons varies considerably (δ_{NH} = 8.7–8.8 p.p.m. in $CDCl_3$ for X = Cl,[12] and 10.2 p.p.m. in DMSO for X = CH_3 [119]), which

indicates the absence of strong hydrogen bonding [structures (XLIII) and (XLIV) with a weaker intramolecular hydrogen bond or with an intermolecular hydrogen bond].

The participation of the NH proton in rapid intramolecular tautomeric conversions (29) in "red" formazans was demonstrated by means of ^{1}H NMR with isotopically enriched samples.[117,118,121] When N(1) = ^{15}N the NH proton appears as a double with $^1J_{^{15}N-^1H}$ = 46–47 Hz, and when N(1) = N(5) = ^{15}N it appears as a triplet with the same magnitude of spin-spin coupling constant. Since the coupling constant observed has half the magnitude of that typical for structures of a similar kind, the only reason for its decrease could be the participation of the NH proton in alternate formation of an N–H valence bond first with N(1) then with N(5) as part of the tautomeric intrachelation process (29) (a spin-spin interaction does not occur in an N...H hydrogen bond).

Our view has been expressed that the halving in value of $^1J_{^{15}N-^1H}$ can, in principle, be caused not only by process (29) but also by the formation of the mesomeric structure (XLIIb) instead of the limiting tautomeric forms (XLIIa) and (XLIIc).[118] This proposal can be rejected when taking into account the findings of one study,[117] in which the structural factors causing a displacement of equilibrium (29) in either direction were investigated on triarylformazans as a model. When X = C_6H_5 and N(1) = ^{15}N, introduction of a substituent into the *para* position of one of the aromatic rings (Ar′) (the other ring Ar″ = C_6H_5) has a marked effect on the constant $^1J_{^{15}N-^1H}$; when Ar′ = p-$CH_3OC_6H_4$, it amounts to 86.5 Hz, while when Ar′ = p-$O_2NC_6H_4$ it becomes equal to zero. Thus, electron-donor substituents at the *para* position of one of the aromatic rings promote such a displacement of equilibrium (29) that the azo group is stabilised next to this ring. Electron-withdrawing substituents have the opposite effect. In proposing mesomeric structure (XLIIb) these results would have no rational explanation. The tautomeric process (29) is a low-energy one since it is not possible to slow it down noticeably even on cooling the solutions.[118,119,121] This fact indicates the importance of establishing the position of this and similar equilibria by means of NMR spectroscopy. Apart from the one study,[117] related to this are two reports,[123,124] in which appropriate ^{13}C NMR data is presented.

IX. COMPLEX COMPOUNDS OF AZO DYES WITH METAL IONS

Metallated and metal-containing hydroxyazo dyes constitute a fairly large and essentially important group of dyes. The NMR data relating to their complexes with metal ions[28–32,74–76,105,124] are still sparse, very incomplete, and provide only a few answers to certain structural problems.

In particular, data relating to the ^{1}H NMR spectra of complexes of 1-(2-hydroxybenzeneazo)-2-naphthol (XXIXa) with certain metal ions have been reported.[32] The absence of details in the interpretation of the spectra makes it difficult to discuss these data, but the conclusion of the authors[32] about the quinone hydrazone form of the ligand in the complex with Zr(IV) of composition 1 : 2 was not confirmed by the subsequent application of ^{13}C NMR spectroscopy.[75] It was established that the azo form of the ligand is preserved on complex formation with these ions.

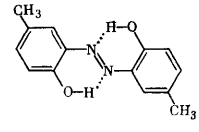
By means of ^{1}H,[28–31,76] ^{15}N,[105] and ^{13}C[76] NMR spectroscopy it was possible to study the isomerism for two types of complex based on 2,2′-dihydroxyazobenzene compounds with a wide variety of structure in which the dye is a tridentate O,N,O ligand—octahedral Co(III) complexes of the type (O N O)$_2$Co,[28–31,76] and square planar Pt(II) and Pd(II) complexes of the form (O N O)MB (B is pyridine or another additional ligand that has basic properties).[31,76,105]

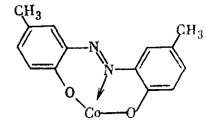

(XLVa)


(XLVb)

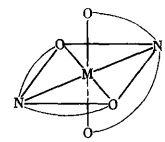
Some authors[31,76,105] used NMR spectroscopy methods to study, in particular, the differences between the isomers (XLVa) and (XLVb) of square planar Pt(II) and Pd(II) complexes when the left- and right-hand sides of the 2,2′-dihydroxyazobenzene dye molecule are nonequivalent.

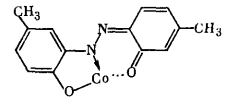
A series of studies[28–31,76,105] constitutes the start of an extensive and technically important trend in NMR investigations that would be simply impossible without polynuclear NMR spectroscopy. Possibly because of the difficulties in interpreting ^{1}H and ^{13}C NMR spectra for complex structures, the authors limited themselves to discussion of only isolated NMR signals. The contemporary state of NMR spectroscopy permits the study of complex compounds—metal-containing dyes or compounds that are metallated in the dyeing process—with complete interpretation of the spectra.


(XLVI)


(XLVIIa)

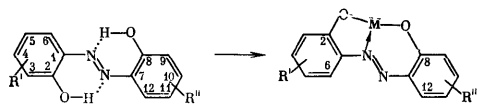
To what extent this step is important can readily be seen from the studies[28,29,76] in which NMR spectroscopy was used to study octahedral Co(III) complexes with two ligands attached to one metal ion. The complex with substituted 2,2′-dihydroxyazobenzene (XLVI)[28] was studied by ^{1}H NMR. On replacement of two protons by metal the initial symmetrical dye (XLVI) becomes asymmetric in the coordination unit (XLVIIa), and in the spectrum of the complex instead of one there are two methyl signals ($\Delta\delta_{CH_3}$ = 0.1 p.p.m.) and two H(6) signals (Δd_H = 0.08 p.p.m.). Since only one set of ^{1}H NMR occurs in the spectrum of the complex, the solution to the problem concerning the configuration process of two coordination units of (XLVIIa) is considerably simplified—there are two planar (XLVIIa) fragments arranged perpendicular to each other in the octahedron [structure (XLVIII)].


(XLVIII)


(XLVIIb)

Thus the nonequivalence of the left- and right-hand sides of coordination unit (XLVIIa) for the symmetrical initial ligand (XLVI) follows from the very fact that coordinated and uncoordinated nitrogen atoms exist in it. In two studies,[28,29] where the discussion concerns complexes of Co(III) with an asymmetric 2,2′-dihydroxyazobenzene ligand, namely, with the possible formation of isomers and a more complex NMR pattern, the authors attribute the quinonoid structure (XLVIIb) to one of the sides of the ligand in the

coordination unit instead of the azoid structure (XLVIIa). Although this is not essential for the construction of the octahedral complex (XLVIII), this hypothesis in itself was not supported by the ^1H NMR spectra. The results of subsequent study of ^{13}C NMR spectra led the authors to the conclusion that coordination unit (XLVIIa) containing an azo structure was occurring.[76]



(XLIX)

A method for identifying the signal that corresponds to the C(6) carbon atom was proposed.[76] When coordination unit (XLIX) is formed, out of the two atoms C(6) and C(12) only atom C(6) changes its spatial position relative to the N=N bond, occupying a *cis* position relative to the N=N double bond after rotation about the C–N bond. Consequently, after rotation and subsequent complex formation (OH → OM), the signal corresponding to C(6) must be shifted upfield by an order of magnitude of 9 p.p.m. (plus or minus an addition shift due strictly to the effect of complex formation). The actual values of the upfield shift depending on the metal amount to: 13–14 p.p.m. for Pd(II) and Pt(II); 14–15 p.p.m. for Co(III). Thus, the upfield shift due to complex formation (as a result of replacing H^+ by M^{n+} and the change in angle values when going from a six-membered ring involving hydrogen bonding to a five-membered ring with M^{n+}) for C(6) amounts to 4–5 p.p.m. for Pd(II) and Pt(II) and 5–6 p.p.m. for Co(III). However, it may be assumed that this additional upfield shift is mainly due to transformation of the six-membered hydrogen bonded ring to the five-membered coordination ring since when complex formation occurs with preservation of a six-membered ring the C(6) signal is shifted downfield only by ~2.5 p.p.m.

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Analytical Gas Chromatography of Volatile Metal Complexes

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The recent advances in the gas chromatography of volatile metal complexes such as β-diketonates, adducts of β-diketonates with neutral donors, dialkyldithiocarbamates, β-ketoaminates, and other compounds are examined. Attention is mainly focused on methods for determining trace metals, capillary chromatography, chromatography in ligand vapour, and studies on the abnormal behaviour of metal chelates on a chromatography column.
The bibliography includes 138 references.

CONTENTS

I.	Introduction	956
II.	Metal β-diketonates	956
III.	Adducts of β-diketonates with neutral donors	958
IV.	Complexes of metals with nitrogen- and sulphur-containing ligands	958
V.	Gas chromatographic separation of metal chelates on capillary columns	961
VI.	Gas chromatography of metal β-diketonates in ligand vapour	963
VII.	Behaviour of metal chelates on a chromatography column	963
VIII.	Gas chromatographic determination of trace metals	964

I. INTRODUCTION

The present review covers the period from the middle of 1975 to the end of 1986. During these 11 years there was a marked development of research into the gas chromatography of volatile metal complexes. About 120 original articles, a number of reviews,[1-17] and two monographs[18,19] which are completely or partly devoted to this topic have been published. Since in the preceding five-year period (1970–1975), which was covered in a previous review,[5] about 70 articles, including 7 reviews, were published, it is evident that the growth rate of research in this field has remained approximately the same. The main trends have also not changed significantly; these are either a comparative study of the properties of new volatile metal compounds that are united by some common feature (mostly these are complexes of a number of metals with one or more ligands or complexes of a single metal with a number of ligands) or better separation and improved sensitivity for determining those complexes already known.

Research into new volatile metal compounds has been conducted with considerable vigour. In addition to the traditional β-diketonates and β-ketoaminates, a large number of adducts of metal β-diketonates with neutral donors have been synthesised and studied as also have dialkyldithiocarbamates, dialkylthiophosphates, and analogues of β-diketonates that contain donor atoms of oxygen, sulphur, and nitrogen in different combinations. Several studies on the gas chromatography of metalloporphyrins have appeared.

As regards chromatographic experimental technique, mention can be made of the further development of gas chromatography using carrier gas into which the vapour of a ligand is introduced (GCLV) as well as the appearance of a promising new field—chromatography of metal chelates on glass and quartz capillary columns.

As before the most popular detectors are the flame ionisation detector and electron capture detector, although in some studies new ones such as microwave plasma, nitrogen-phosphorus, and flame photometric detectors are used. The heat-transfer detector is now rarely used. The use of chromatography–mass spectrometry has become quite common.

A considerable section of research is devoted to the practical application of gas chromatography in determining small traces of metals in a particular substance. Mention can be made here of the increase in the number of determinable metals and the improvement in sensitivity for determining many of them.

II. METAL β-DIKETONATES

β-Diketonates were the first volatile metal complexes to be used in gas chromatography. During the last two decades they have been thoroughly studied. However, even at the present time this class of compounds continues to attract the attention of research workers. Volatile β-diketonates of about forty metals have been synthesised. The most suitable for gas chromatography are metal complexes with β-diketones that contain *tert*-butyl and perfluoroalkyl substituents. The attraction in using β-diketonates for analysis lies in the fact that in most cases the ion being determined can readily and rapidly be converted quantitatively into a volatile chelate by extracting it from aqueous solution with a solution of the appropriate β-diketone in a non-polar organic solvent. However, the β-diketonates of many metals are kinetically labile and have insufficient thermal stability, which leads to their partial decomposition and irreversible adsorption on the chromatography column. As a result, abnormal effects occur during separation which prevent the widespread use of β-diketonates in quantitative analysis.[18]

Therefore, only the most stable β-diketonates of chromium(III), aluminium(III), beryllium(II), cobalt(III), and a few others are of practical use.

Numerous attempts using different methods to expand this list have not produced tangible results. An exception to this is the gas chromatography in ligand vapour (GCLV) proposed by Japanese authors, which will be examined below. However, this method is technically complex and excludes the use of the most common detectors (flame ionisation and electron capture), which considerably reduces its practical value.

1. Non-fluorinated β-Diketonates

Only a few studies in recent years have been devoted to non-fluorinated β-diketonates. The chromatographic behaviour of chromium and beryllium acetylacetonates and chromium propionylacetonates on different liquid phases has been investigated and it has been shown that beryllium acetylacetonate decomposes to a considerable extent on chromatography columns.[20] The satisfactory separation of chromium, aluminium, and cobalt(III) acetylacetonates on a column (1 m × 4 mm) with 5% Silicone OV-17 on Chromosorb W using a programmed increase in temperature from 190 to 250 °C (8 K/min) has been reported.[21,22] The gas chromatographic determination of aluminium as its acetylacetonate in soils has been reported[23] and a method has been developed[24] for determining copper in catalysts (also in the form of its acetylacetonate). The quantitative analysis of certain rare earth elements in the form of dipivaloylmethanates has been carried out.[25] One study,[26] in which for the first time gas chromatographic separation of rare earth acetylacetonates was achieved, is of interest. However, the gas chromatographic properties of these complexes are far from perfect and the separation of chelates of adjacent rare earth elements was not achieved. It was found that rare earth β-diketonates can react with vaporised β-diketonates, including acetylacetone (AA), in both the gas and condensed phases to give mixed ligand complexes.[27]

The use of non-fluorinated metal β-diketonates in gas chromatography is not likely to be of future interest. Only dipivaloylmethanes, which are of interest for the separation of rare earths and other metals, constitute an exception to this.

2. Fluorinated β-Diketonates

A considerably larger number of articles have been devoted to the volatile metal chelates with fluorine-containing β-diketonates. The chromatographic behaviour of vanadium(III) and vanadyl chelates with trifluoroacetylacetone (TFA), pivaloyltrifluoroacetone (PTA), and heptafluorodimethyloctanedione (HDO) has been studied.[28,29] It was shown that the chromatographic properties of vanadyl chelates were unsatisfactory. In addition to the usual abnormal effects (adsorption of the first samples of chelate on the column and a non-linear calibration curve at low concentrations), a partial reduction of vanadium(IV) to vanadium(III) also occurred on the column.

Vanadium(III) β-diketonates have better chromatographic properties. Particularly good results were obtained when studying a vanadium(III) chelate with HDO, which displayed virtually no abnormal effects. Volatile chelates of molybdenum(V) and (IV) with β-diketones that contain terminal CF_3, C_3F_7 or $C(CH_3)_3$, CH_3, thienyl, furyl, C_6H_5, and camphorate groups have been synthesised.[30] The authors claim that these chelates can be used in gas chromatography and also for improving the sensitivity of the atomic absorption method for analysing molybdenum. The thermal stability and chromatographic behaviour of chelates of copper and erbium with ten β-diketones that contain terminal CF_3, $C(CH_3)_3$, C_6H_5, and CH_3 groups have groups have been studied. As was to be expected almost all the copper complexes proved to be suitable for gas chromatography but the thermal stability of the erbium chelates was in most cases insufficiently high.

The chromatographic behaviour of complexes of aluminium, vanadium(III), chromium(III), iron(III), manganese(III), cobalt(III), and copper(II) with β-diketones containing terminal CF_3, C_2F_5, C_3F_7, CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$ groups has been studied[32] on glass columns with Silicone SE-30 deposited on different solid supports.

Chelates of thallium(I) with PTA and HDO and thallium(III) with TFA, PTA, and HDO have been synthesised.[33] All these chelates can be satisfactorily chromatographed in microgram quantities on a glass column (75 × 0.4 cm) with 5% Silicone DC-550 on Chromatotone N AW DCMS at 170 °C, and thallium(I) compounds are retained to a considerably greater extent than thallium(III) compounds. Partial decomposition of the compounds studied on the column was recorded.

In a number of studies into the behaviour of volatile β-diketonates, compounds labelled with radioisotopes have been used. Thus, Buchtela et al.[34] chromatographed aluminium and chromium acetylacetonates and a number of rare earth complexes with HDO using ligands labelled with tritium. A flame ionisation detector and proportional counter were used for detection, and in the latter case it was possible to record a low detection limit for chromium ($\sim 10^{-15}$ g).

The gas chromatographic determination of chromium labelled with ^{51}Cr as a complex with hexafluoroacetylacetone (HFA) has been reported.[35] A gas-flow counter was used for detection. High accuracy in determining the isotope ratios for a number of alkaline-earth and transition metals (magnesium, calcium, chromium, iron, nickel, copper, cadmium, zinc) was achieved with the use of gas chromatography–mass spectrometry.[36] The metals were converted to complexes with TFA, PTA, or HDO or to diethyldithiocarbamates (DEDTC); separation was effected on a glass column with 1% or 6% Silicone SE-30 on Gas-Chrom Q. The authors maintain that the method is suitable for determining alkaline-earth and transition metals in natural materials using a mass spectrometric version of isotopic dilution.

The separation of geometric isomers of molybdenum(III) trifluoroacetylacetonates has been carried out.[37] The isolated preparatively pure complexes were identified from their electronic spectra, solubility, and melting points.

In one study[38] the suitability of a nitrogen-phosphorus detector for chelates with AA, TFA, and HFA was investigated. The sensitivity of the nitrogen-phosphorus detector proved to be comparable to that of the electron capture detector.

Volatile chelates of zirconium(IV) and hafnium(IV) with AA, TFA, and HFA have been synthesised, and their thermal stability and suitability for gas chromatography investigated.[39] Mikhailenko and Sereda[40] synthesised chromium(III) chelates with fifteen different β-diketones, carried out thermogravimetric analysis of these compounds, determined their dipole moments, and found that there was no correlation between the magnitude of the dipole moments and the retention times of the chelates studied. A number of thermodynamic values specific to the gas–liquid equilibrium for several stationary phases were also determined.

Several studies are devoted to the application of gas chromatography of β-diketonates for the practical analysis of metals in various substances. There have been reports on the determination of beryllium as a complex with TFA in natural and waste water[41] and also in tap water and uranium oxide[42] and in metal alloys.[43] The determination of aluminium and chromium (also as chelates with TFA) in aqueous solution at concentrations down to $10^{-6}-10^{-7}$ g/litre has been reported,[44] and the determination of vanadium in polymers, complex compounds, and petroleum has been described.[45,46] The determination of small quantities of chromium in various substances has also been the subject of studies.[47-51]

A method for determining traces of ruthenium in car exhaust gases in the form of a trifluoroacetylacetonate has been developed.[52] The detection limit for ruthenium reached 2.4×10^{-13} g. A method for determining aluminium and copper as complexes with PTA in glasses and alloys has been reported.[53]

III. ADDUCTS OF β-DIKETONATES WITH NEUTRAL DONORS

In recent years research workers have shown increased interest in adducts of metal β-diketonates with neutral donors. This applies particularly to complexes with HFA. As was indicated,[18] metal chelates with HFA were not of particular interest for a long time because of the tendency of HFA to react with water to give tetrahydroxy compounds incapable of forming complexes with metals. It transpired, however, that in the presence of neutral donors such as dibutyl sulphoxide (DBSO), tributyl phosphate (TBP), etc., adducts can be synthesised (usually containing one or two donor molecules) by normal extraction from aqueous solutions.[54,56,57]

In this connection a number of studies on the gas chromatography of compounds of this class have recently appeared. Thus, the gas chromatographic behaviour of adducts of manganese(II), iron(II), cobalt(II), and nickel(II) hexafluoroacetylacetonates with TBP and DBSO has been investigated.[54] Preliminary experiments showed that when TBP was used as a neutral donor the chromatographic peak from the donor was superimposed on the adduct peaks, so the studies were mainly conducted on adducts with DBSO. The metal ions were extracted from aqueous solutions at pH 5.0–5.5 with a solution of a mixture of HFA and DBSO in cyclohexane. All the adducts obtained by this method had the composition ML_2. .2DBSO (where M is metal ion, L is HFA anion). Separation was carried out on a glass column (25. × 0.3 cm) with 5% Dexsil-300 on Chromosorb W HP. The packing was silanised directly in the column. It was found that the concentration of DBSO in solution had little effect on the stability of the adducts. For all the adducts adsorption effects of the first samples of complex in the column, which are common for simple β-diketonates, and a column "memory" effect occurred. The presence of the respective metals in the adducts was confirmed by atomic absorption spectroscopy.

The behaviour of adducts of manganese(II), iron(II), cobalt(II), and copper(II) β-diketonates with neutral donors such as dimethylformamide (DMF) and tributylphosphine oxide (TBPO) has been studied.[55] A study of the thermal properties of anhydrous and hydrated manganese(II) β-diketonates and adducts of manganese(II) hexafluoroacetylacetonate with DMF and TBPO showed that introduction of a neutral donor into the molecule of complex considerably increased the thermal stability of the molecule and made it possible to sublime the complex almost without decomposition at 100–130 °C. Satisfactory chromatograms were obtained for adducts of hexafluoroacetylacetonates of the metals listed above for DMF and TBPO on a glass column (125 × 0.4 cm) with 5% Silicone SE-30 at 100 °C and their retention times were determined.

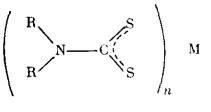
A radioactive indicator method was used to study the extraction of scandium, chromium(III), manganese(II), iron(III), cobalt(II), copper, zinc, yttrium, silver, cadmium, lanthanum, cerium(II). europium(III), ytterbium(III), mercury(II), thorium(IV), uranium(IV) and (VI), vanadium(IV), and americium(III) ions from aqueous solutions at pH 3.0–3.3 with cyclohexane solutions containing stoichiometric quantities of HFA and neutral donors such as *n*-butylamine, isobutylamine, *tert*-butylamine, TBP, TBPO, and trioctylphosphine oxide (TOPO).[56] The adducts obtained were studied thermogravimetrically. It transpired that the adducts with TBPO had the highest volatility. The chromatographic behaviour of these adducts was studied on different packings with programmed temperature change in the range 180–250 °C. The elution temperatures were found for a number of adducts of metal hexafluoroacetylacetonates with TBPO.

In a later study the same authors[57] studied adducts of rare earth hexafluoroacetylacetonates with TOPO, TBPO, TBP, tetrahydrofuran, *n*-butylamine, and dodecylamine. In this case adducts with TBPO also had the best properties as regards gas chromatography. Chromatographic separation was carried out on glass columns (60 × 0.4 cm or 90 × 0.4 cm) with 10% Silicone OV-101 or Dexsil-300 on Chromosorb W HP. The temperature was raised from 180 to 250 °C at a rate of 2 K/min, and a flame ionisation detector was used. Out of all the rare earth adducts the peaks from samarium, terbium, dysprosium, holmium, erbium complexes were effectively resolved on the chromatogram, the remaining peaks were only partially resolved.

IV. METAL COMPLEXES WITH NITROGEN- AND SULPHUR-CONTAINING LIGANDS

1. Dialkyldithiocarbamates

Recently chromatography researchers have shown increased interest in dialkyldithiocarbamates (DADTC) of metals with the general formula:



where M is a metal ion and *n* is its charge. The first report on the chromatographic separation of copper, nickel, and zinc DADTC appeared in 1969,[58] but a systematic study of the suitability of compounds of this class for gas chromatography has only started since 1975. Not long afterwards di(trifluoroethyl)dithiocarbamates (DTFEDTC), which have a higher volatility and better chromatographic properties, were synthesised.[59]

Non-fluorinated DADTC are less volatile than β-diketonates and are usually chromatographed at higher temperatures (in the region of 170–230 °C). Although there are not infrequent indications in the

literature that metal DADTC complexes partially decompose on columns or during thermogravimetric studies, there are virtually no reports about the type of abnormal effects that occur when using β-diketonates, such as adsorption of the first samples of chelate on a new column or the column "memory" effect. This is probably due to the greater kinetic stability of dialkyldithiocarbamates, which inhibits the rapid exchange of ligands between complexes. Satisfactory chromatographic properties are mainly displayed by DADTC chelates of bivalent ions (copper, nickel, zinc, and others), but some authors also managed to chromatograph complexes of chromium(III), iron(III), gold(III), thallium(I), antimony(III), bismuth(III), indium(III), and rhodium(III).[62,67-69,73,105,107]

DADTC complexes are even more convenient than β-diketonates as regards their practical application. A quantitative conversion of the ions being determined to the corresponding complexes is carried out by extracting them from aqueous solution as in the case of β-diketonates. But while the chromatographic determination of small quantities of metals as β-diketonates is only possible using expensive β-diketones with perfluoroalkyl substituents, in the case of DADTC perfectly satisfactory results are often obtained using readily available diethyldithiocarbamates (DEDTC).

In one study[60] the chromatographic behaviour of seven different nickel(II) DADTC that contained CH_3, C_2H_5, C_3H_7, H, *iso*-C_4H_9, and C_5H_{12} groups as terminal substituents was examined. The best results were obtained with diethyl derivatives. In the chromatogram of a mixture of diethyl, di-*n*-propyl, and di-*n*-butyl complexes of nickel shown in this study[60] there were no peaks from chelates with mixed ligands, which is confirmation of the kinetic stability of dialkyldithiocarbamate complexes.

The separation of nickel, copper, and zinc diethyldithiocarbamates on a glass column (60 × 0.3 cm) with 3% Silicone OV-25 at 260 °C has been reported.[61] The same authors[62] carried out the separation of lead(II), nickel, copper, cadmium, and zinc DEDTC under approximately the same conditions as well as di(trifluoroethyl)-dithiocarbamates (DTFEDTC) of nickel, copper, and zinc (in the same mixture) and bismuth(III), antimony(III), lead(II), cadmium, nickel, and zinc (in another mixture) at temperatures of 240 °C and 185 °C respectively on a column with 5% Silicone SE-30 on Chromosorb W. It was possible to determine a number of metal cations down to concentrations of 6×10^{-5}% using a flame ionisation detector.

The possibility of detecting small quantities of zinc, cadmium, nickel, mercury(II), and lead(II) DEDTC using an electron capture detector with ^{63}NI was examined, and it was found that the detection limit for lead complexes was 6 ng and 2–4 ng for the remaining complexes in a sample.[63] In some cases the peaks from the pure zinc and cadmium chelates were split. The explanation for this given by the authors is that the respective complexes are present in the system in both the monomer and dimer forms. However, this phenomenon was only observed in this study. The determination of zinc, copper, and nickel as their DEDTC complexes in marine residues and in other substances has been reported.[64,65]

In one study[66] the chromatographic behaviour was examined and mass spectra obtained for copper, cadmium, cobalt, zinc, and nickel DEDTC and partial decomposition of the copper, cobalt, and cadmium complexes was detected on a column with Silicone SE-30 using different solid supports. For the quantitative determination of nickel and zinc DADTC the use of a column with 2% Silicone SE-30 on Chromosorb G AW DMCS or on Gas-Chrom Q was recommended. For the first time the separation of a number of DADTC complexes was also carried out on a glass capillary column of length 31.4 m with Silicone OV-101. Mass spectrometric analysis showed that with an increase in length of alkyl substituents in a DADTC molecule the degree of decomposition of the chelate on evaporation increased.

A method for determining chromium(III) and chromium(VI) in aqueous solution by their combined presence as DTFEDTC complexes has been developed.[67] The best results were obtained on packed columns with 3% Silicone OV-25 at 160–210 °C or Silicone OV-101 at 190–230 °C. The minimum concentration of chromium that could be detected was 5×10^{-5}%. Cobalt(II), nickel, zinc, cadmium, lead(II), copper, and iron(III) ions inferred with the determination. Similar methods have been reported in other studies.[68,69]

Meyer and Neeb[70] chromatographed nickel and cobalt DTFEDTC on packed columns with Silicone OV-101 (3%) deposited on different supports. When Chromosorb W HP was used on a glass column (90 × 0.25 cm) with programmed temperature change (2 K/min) in the range 135–200 °C, using a flame ionisation detector it was possible to detect down to 1×10^{-6}% nickel and cobalt in solution in the presence of tenfold quantities of copper, cadmium, and zinc and thousandfold quantities of iron.

The determination of rhenium(IV), (V), and (VII) in aqueous solution as DADTC complexes with ethyl and phenyl terminal groups has been reported.[71] The complexes were extracted with chloroform from hydrochloric acid solutions. Separation was carried out on a glass column of length 0.6 m with 5% Silicone SE-30 on Chromatone N AW DMCS.

A comparison of the suitability of different solid supports for the quantitative gas chromatographic determination of nickel and zinc DEDTC [72] showed that Chromosorb W HP and Chromatone N-Super had the best properties and that Chromosorb G was the least suitable.

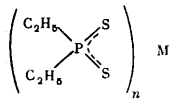
One study[73] is concerned with the determination of noble metal ions [gold(III), platinum(IV), palladium(II), rhodium(III), and iridium(IV)] as complexes with DTFEDTC. It should be noted that this is the first report on the quantitative gas chromatographic determination of gold. Separation was carried out on a glass column (80–100 × 0.2 cm) with 3% Silicone OV-3 on Chromosorb G AW DMCS at 210–220 °C using an electron capture detector with ^{63}Ni. The sensitivity for determination was comparable to the sensitivity of atomic absorption spectroscopy with electrothermal atomisation and in a number of cases even exceeded the latter.

In a study of the chromatographic behaviour of copper and nickel complexes with fifteen different DADTC on OV-101, NGA, and OV-225 liquid phases it was found that the shortest retention times were typical for chelates with short alkyl terminal groups if chromatography was carried out on a polar liquid phase.[74]

One study[75] is concerned with developing a method for determining trace metals as DEDTC complexes in aqueous solution. Analysis of small quantities of nickel, copper, zinc, cadmium, mercury, lead, and cobalt on columns of length 30–60 cm containing mixures of siloxane liquid phases—SE-30, QF-1, OV-101—on Gas-Chrom Q and Chromosorb W HP showed that lead, cadmium, and mercury DEDTC displayed signs of decomposition during the experiment. When a flame ionisation detector was used the limiting dilutions for the different metals ranged from 17 to 300 ng/ml. It is interesting to note that the authors carried out the experiments not only on glass columns but also on metal columns and found that in the latter case the detection limits increased by a factor of about one and a half.

2. Dialkyldithiophosphinates and Dialkyldithiophosphates

Kleinman and Neeb[76] synthesised diethyldithiophosphinates (DEDTP) of zinc, cadmium, cobalt, nickel, and lead with the general formula

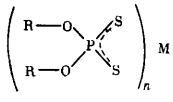


Thermogravimetric studies showed that all of the compounds obtained partially decomposed on sublimation (the non-volatile residue amounted to 2–11%). Nevertheless, the authors[76] prepared chromatograms of several mixtures of these compounds, including mixtures of zinc, cadmium, nickel, and lead DEDTP. Separation was carried out on a glass column (78 × 0.3 cm) with 3% Silicone OV-17 on Chromosorb N AW. Less satisfactory results were obtained when SE-30, OV-101, and Apiezon L were used as liquid phases. The cobalt complex was apparently not suitable for gas chromatography.

Somewhat later[77] the chromatographic behaviour of DEDTP complexes of the same metals was studied on columns with different silicone liquid phases on Chromosorb Q. The authors maintained that the lead chelate rapidly decomposed in solution on exposure to light. A method for determining traces of cadmium in aqueous solution at concentrations down to 3×10^{-6}% in the presence of a hundredfold excess of zinc is reported in the study.

The gas chromatographic behaviour of nickel, zinc, and cadmium di-isopropyldithiophosphinates under much the same conditions has also been reported[78] and the partial decomposition of the cadmium complexes was recorded. It was possible to detect these chelates in solution when their concentration was $\sim 2 \times 10^{-6}$ moles/litre.

Two studies[79,80] are devoted to the gas chromatography of

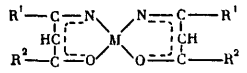


volatile dialkyldithiophosphates. From among the dimethyl- and diethyl-dithiophosphate complexes of nickel, palladium, and platinum, the di-*n*-propyldithiophosphate complexes of nickel and palladium, and the di-isopropyldithiophosphate chelates of zinc, nickel, palladium, platinum, copper, mercury(II), chromium(III), rhodium(III), cobalt(III), gold(III), ruthenium(III), and iridium(III) that were synthesised only the dimethyl- and di-isopropyl-dithiophosphates of nickel, palladium, platinum, chromium(III), and rhodium(III) proved to be suitable for gas chromatography.[79] The best chromatograms were obtained on columns with Silicone OV-101, SE-30, and PS-300 on Gas-Chrom Q or Chromosorb 750 at 150–180 °C.

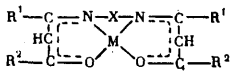
The later study[80] described the chromatographic behaviour of diethyldithiophosphates of a number of metals on packed and capillary columns. When a flame ionisation detector was used the detection limits reached 10^{-11}–10^{-12} g of metal.

3. β-Ketoaminates and Metal Complexes with Ligands Containing S, O and S, N Donor Pairs

Bidentate and tetradentate β-ketoaminates (sometimes also called β-aminovinylketones, β-ketoimines, and Schiff bases) are formed by condensation of β-diketones with mono- or di-amines. They form chelate complexes with many metal ions. It is mainly β-ketoamine complexes with bivalent copper ions and metal ions of the nickel group that are suitable for gas chromatography:[18]



bidentate β-ketoamine complex



tetradentate β-ketoamine complex (X—hydrocarbon chain)

When considering bidentate β-ketoamines as ligands there is practical interest mainly in ketoamines obtained by condensation of diketones with ammonia, since metal complexes with N-alkyl-substituted β-ketoamines are thermally unstable and tend to hydrolyse. Unfortunately, even the most stable metal chelates with bidentate β-ketoamines fairly readily eliminate ligands on heating. As a result of this they usually decompose on the column during chromatography, which gives rise to abnormal effects.[18]

Complexes with tetradentate β-ketoamines are in most cases more stable and have better chromatographic properties despite their lower volatility. Under optimum conditions using an electron capture detector, such chelates can be detected using chromatography down to 10^{-12} g. Fluorinated complexes have particularly good properties. However, their practical application in analysis is made difficult by the extremely low solubility of fluorinated tetradentate β-ketoamines in water, which inhibits the use of the usual extraction methods for quantitative conversion of a metal being determined into the respective complex. The problems in the analytical use of β-ketoaminates have been examined in detail in a monograph.[18]

Attempts to use salicylaldiminate complexes of copper, nickel, and zinc for gas chromatography did not give favourable results.[18,81]

The thermal stability and chromatographic behaviour of 2-picolylalkylketonates [82] and 2-picolyltrifluoromethylketones [83] of beryllium, copper, zinc, nickel, and chromium were studied. It was found that the chelates of all the metals investigated apart from chromium were suitable for quantitative gas chromatographic analysis. However, the detection limits of these complexes were not stated.

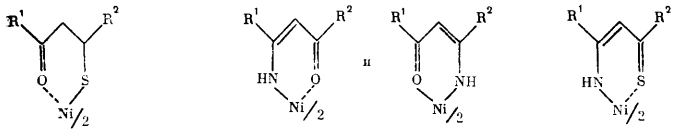
The volatility and chromatographic behaviour of vanadyl,[84–87] copper, nickel,[84,86,87] and iron(III) [88] complexes with certain Schiff bases were studied. Satisfactory results were obtained when 1,1,1,1′,1′,1′-hexafluoro-4,4′-(1-methylethane-1,2-diyldi-imino)*bis*-(pent-3-en-2-one) [86] and 2,2,2′,2′-tetramethyl,5,′-(ethane-1,2-diyldi-imino)*bis*(hex-4-en-3-one) [85] were used as ligands for the determination of nanogram quantities of copper, nickel, and vanadium in petroleum and biological materials.

The simultaneous determination of copper and nickel as complexes with 1,1,1-trifluoro-1′,1′,1′-trimethyl-4,4′-ethane-1,2-diyldi-imino)*bis*(pent-3-en-2-one) in aqueous solution at concentrations of 0.02–0.12 mg/ml has been reported.[89]

For the gas chromatographic determination of iron(III), its complexes with hexadentate ligands—4,4′,4″-(neopentane-1,3,4-triyltri-imino)*tris*(pent-3-en-2-one) and 4,4′,4″-(cyclohexane-*cis*,*cis*-1,3,5-triyltri-imino)*tris*(pent-3-en-2-one)—were used.[88] It was possible to

detect down to 1×10^{-10} g of iron on a column (46 × 0.65 cm) with 3% Silicone OV-101 on Gas-Chrom Q at 200 °C using a flame ionisation detector.

Several studies have been published that are devoted to a comparison of the chromatographic properties of volatile nickel(II) complexes with ligands of analogous structure to β-diketones but containing S, O and O, N pairs as well as S, N [90-93] as donor atoms instead of two oxygen atoms. In these studies 25 compounds of four types were studied:



monothio-β-diketonates (MTBDK) β-aminovinylketonates (AVK) β-aminovinylthionates (AVT)

The terminal groups in the compounds investigated were CH_3, CF_3, $H(CF_2)_2$, $H(CF_2)_4$, C_3H_7, C_2F_5, $C(CH_3)_3$, $CH(CH_3)_2$, n-C_4H_9, and C_6H_5 in different combinations. The complexes obtained were chromatographed on glass columns (1 m × 3 mm) using a constant recombination rate detector. Tests on different packings showed that the best results were given by Chromatone N-Super with 3% Silicone SE-30. Retention of all the chelates studied increased with an increase in the length of alkyl terminal groups and also when CF_3 was replaced by $H(CF_2)_2$. Introduction of a *tert*-butyl group improved the chromatographic properties of all the complexes. Complexes with phenyl substituents were not eluted at all or were eluted with a very long retention time.

Nickel monothio-β-diketonates were eluted at 190–210 °C giving asymmetric peaks in all cases. Aminovinylketonates had greater volatility than the corresponding MTBDK complexes and were eluted from the same column at 140–160 °C. Under the experimental conditions, AVK complexes that contained a fluoroalkyl substituent on the carbon atom bonded to the amino group had better chromatographic properties than their structural analogues containing an amino group joined to a carboxyl carbon atom. In several cases the characteristic abnormal behaviour of chelates on a column occurred. Despite their lower elution temperature, in most cases the nickel AVK proved to be less stable during gas chromatography than the MTBDK complexes. Nickel AVT had the best chromatographic properties. Like MTBDK, they were eluted at high temperatures (in the region of 200 °C), but they displayed virtually no abnormal effects and gave symmetrical peaks. The detection limit for these chelates reached 2.5×10^{-10} g.

In one study[94] the thermal stability and chromatographic behaviour of complexes of copper, nickel, zinc, cadmium, platinum, and palladium with 4,4'-(ethane-1,2-diyldi-imino)*bis*(pent-3-ene-2-thione) and copper and nickel complexes of 4-[(3-oxo-1-methylbut-1-enyl)-aminoethylamino]-pent-3-ene-2-thione were studied and the possibility of simultaneous gas chromatographic determination of copper, nickel, and zinc as such complexes was demonstrated. Out of the compounds studied only the cadmium complex proved to be thermally unstable.

V. GAS CHROMATOGRAPHIC SEPARATION OF METAL CHELATES ON CAPILLARY COLUMNS

Although the gas chromatography of metal chelates has been in existence for over 30 years, the first studies on the separation of chelates on capillary columns were only published in 1979. This may have been due to the lack of success in the early attempts to use metal capillary columns for this purpose. There is nothing surprising in this as even when glass and quartz capillary columns, which are much more inert in the chemical sense, are used it is only possible to chromatograph some of the most stable β-diketonates—chelates of chromium, aluminium, beryllium, copper, and a few other metals. The range of metal dialkyldithiocarbamates that can be separated on capillary columns is more extensive, which is probably due to their kinetic stability. Recently, some dialkyldithiophosphates and metal complexes with Schiff bases and porphyrins have also been separated by this method.

The methods used to separate metal chelates on capillary columns are virtually the same as those used for other high-boiling compounds. The most successful results are obtained on columns of length 5–15 m with polysiloxane deposited or grafted stationary phases. Injection of the sample is carried out both directly into the column and with split flow. A flame ionisation detector is usually employed.

The separation of structural isomers of chromium trifluoroacetylacetonates and mixed ligand complexes of chromium with TFA and HFA as well as a number of copper β-ketoaminates and cyclopentadienyl compounds of manganese and chromium on capillary columns made of stainless steel with a porous layer has been described.[95] Dexsil-300 was used as the stationary phase. The separation of aluminium, beryllium, chromium, and copper trifluoroacetylacetonates has been carried out on glass and quartz capillary columns of length 5–15 m.[96] Sievers and Brooks[97] separated 25 isomeric chromium β-diketonates on a quartz capillary column (30 m × 0.32 mm) with Silicone SE-54.

The chromatographic behaviour of trifluoroacetylacetonates, pivaloyltrifluoroacetonates, and trifluoroacetylisovalerylmethanates of aluminium, beryllium, chromium, copper, cobalt, iron, and nickel has been studied on quartz capillary columns with OV-101, OV-17, and SE-54.[98] In particular, it was possible to separate isomeric aluminium and chromium pivaloyltrifluoroacetonates. The detection limits of the metals when using a flame ionisation detector reached 4×10^{-14}–2.2×10^{-12}g.

The first successful attempt to separate rare earth β-diketonates on the glass capillary column has been reported.[99] Rare earth chelates with PTA were separated on a column (9.5 m × 0.3 mm) with OV-17 stationary phase and a programmed temperature increase (15 K/min) in the range 175–250 °C. It was possible to separate mixtures of Sc–Lu–Er–La, Sc–Lu–Tm–Ho–La, and others. When longer columns were used and silicones SE-30, OV-101, and SE-52 were employed as liquid phases, separation was less good.

The separation of DADTC complexes of iridium, palladium, lead, cadmium, zinc, selenium, rhodium, cobalt, and arsenic was carried out on a glass capillary column (7 m × 0.3 mm) with Silicone OV-101 at 190–255 °C.[100] A flame ionisation detector was used. An attempt to use pyrrolidinedithiocarbamates proved unsuccessful. The use of dipropyl- and dibutyl-dithiocarbamates gave better results;[101] it was possible to separate selenium, zinc, lead, and palladium chelates with a programmed temperature increase (20 K/min) in the range 170–245 °C. Calibration curves remained linear over the range 5×10^{-8}–1×10^{-6} g of chelate. When the content of chelate in the sample was less than 5×10^{-8} g, partial irreversible adsorption on the column occurred.

In one study[102] the chromatographic behaviour of DTFEDTC and di-isobutyldithiocarbamates of nickel, copper, zinc, cadmium, mercury(II), lead(II), and cobalt(III) was investigated. Separation was carried out on short (1–7 m) quartz and glass capillary

columns of internal diameter 0.30–0.32 mm with OV-101, SP-2100 and FFAP as liquid phases using different modes of programmed temperature increase. The best results were obtained when non-polar silicone liquid phases were used. Partial decomposition on the columns was only observed for the zinc chelates. The possibility of gas chromatographic detection of trace amounts of these metals was demonstrated.

More recently the determination of nickel, copper, and cobalt as their di-isobutyldithiocarbamates on capillary columns (3–4 m × 0.3 mm) with silicones SE-52 and SE-54 and a programmed temperature increase from 220–270 °C (30 K/min) has been reported.[103] The detection limits were $2-4 \times 10^{-11}$ g of metal. The method was used to determine metals in sea and tap water.

Sucre and Jennings[96] chromatographed different volatile metal complexes, including DEDTC and DTFEDTC complexes of zinc, copper, nickel, lead, and cobalt. Detection was carried out using flame ionisation, electron capture, flame photometric, and nitrogen phosphorus detectors. Separation was carried out on quartz and glass capillary columns of length 5–15 m with SE-30, SE-52, SE-54, SP-2100, Dexsil-300, and Carbowax 20 M as liquid phases. The best results were obtained on the silicone phases and on Dexsil. When an electron capture was used for the DTFEDTC complexes and a nitrogen phosphorus detector used to determine nitrogen, a sensitivity of $0.2-1.4 \times 10^{-12}$ g/sec was attained, when a flame photometry detector was used to determine sulphur the sensitivity was $0.7-1 \times 10^{-12}$ g/sec.

The determination of trace amounts of zinc, copper, cadmium, mercury, lead, and cobalt as DTFEDTC complexes using capillary glass chromatography at 90–250 °C on Silicone SE-30 with a flame ionisation detector has been reported.[104] The chromatographic behaviour of DTFEDTC complexes of thallium, mercury(II), cadmium, copper, cobalt, nickel, iron, lead, indium, bismuth, palladium, and zinc on glass and quartz capillary columns with Silicone SE-54 and on a capillary column with a chemically grafted phase of DB-5 has been investigated.[105] In one experiment the authors succeeded in separating complexes of thallium, zinc, copper, nickel, cadmium, palladium, cobalt, iron, indium, lead, and bismuth.

Chromatography of small quantities ($3-12 \times 10^{-8}$ g) of DEDTC and DTFEDTC complex of zinc, cobalt, lead, palladium, nickel, and copper on a short quartz capillary column (4.5 – 0.32 mm) with Silicone SE-54 has been carried out.[106] A flame ionisation detector was used. Dipropyl- and di-isobutyl-dithiocarbamates were also studied. Experiments were also carried out using a longer column (15 m), and the temperature was increased to 320 °C by programming. For the non-fluorinated chelates, in most cases it was only possible to obtain satisfactory chromatograms on the short column, and there was no advantage in using dipropyl and di-isobutyl derivatives. When separation was carried out on the long column, satisfactory peaks were obtained only for zinc and nickel DEDTC. The peak from bismuth DEDTC had a distorted shape in all cases.

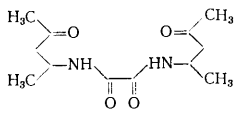
Nanogram quantities of zinc, copper, nickel, palladium, cobalt, chromium, and iron as their DTFEDTC complexes were determined on capillary columns.[107] The metals were extracted from aqueous solution at pH 3.5 with a solution of the ligand in chloroform. The sample was injected into a quartz capillary (5 m × 0.32 mm) installed before the column (15 m × 0.32 mm) with polymethylsiloxane as liquid phase. The column temperature was increased in the range 64–260 °C using a complex program. C_{20} and C_{24} hydrocarbons or palladium chelate were used as internal standards. The calibration curve for the chromium chelate was linear over the range $0.2-20 \times 10^{-9}$ g.

The separation of nickel(II), palladium(II), and platinum(II) DEDTC on a glass capillary column was achieved.[80]

Scheller and Neeb[108] detected chromium, nickel, copper, zinc, cadmium, and cobalt as their DTFEDTC complexes down to 1×10^{-9} g/ml using a flame ionisation detector. When an electron capture detector was used it was possible to improve the sensitivity further by a factor of 100, but the detector used was not adapted to work with capillary columns and as a result the peaks were considerably broken.

A method for the determination of small quantities of copper and nickel DEDTC on a glass capillary column has been reported, and it was characterised by having a large sample (10 μl) injected into a deactivated glass capillary (6 m × 0.32 mm) installed before the column.[109] Normal C_{22} alkane was used as the internal standard. The calibration curves retained linearity over the range $0.25-10 \times 10^{-9}$ g of chelate.

The behaviour of copper, nickel, palladium(II), and vanadyl chelates with a number of tetradentate β-ketoamines including a new type of ligand (tetraketone):



was studied on quartz capillary columns of length 25 m and 6.3 m (internal diameter 0.32 mm) with OV-101, OV-17, PEG-20 M as liquid phases and BP-1, BP-10, and BP-20 chemically grafted phases at 150–240 °C, as well as on packed columns with Silicones SE-30, OV-3, OV-17, OV-25, OV-210, and Dexsil-300 at 200 °C.[110] The best results were obtained on the OV-3 and OV-25 phases. The most suitable carrier gas to use for the capillary columns was hydrogen, which made it possible to work with quite good efficiency at high flow rates. The detection limits for the packed columns using a flame ionisation detector reached $100-140 \times 10^{-9}$ g of chelate, while for the capillary columns the limits were $0.2-2 \times 10^{-9}$ g of chelate. When nitrogen was used as the carrier gas the detection limits were higher by about a factor of 10.

More recently the behaviour of 17 chelates of copper, nickel, zinc, cadmium, platinum, palladium, and vanadyl with a number of tetradentate β-ketoamines and β-aminovinylthiones [111] were studied on five different capillary columns. The rate constants for decomposition of the chelates on the columns were determined along with other parameters. Their values varied from 10^{-1} to 10^{-3} sec^{-1} for the relatively unstable aminovinylthionates and were as low as 10^{-5} sec^{-1} for the stable β-ketoaminates. Enthalpies of solution were also determined for a number of chelates on several different liquid phases.

The gas chromatographic separation of complexes of nickel, copper, vanadyl, and cobalt(II) with etioporphyrin I and octaethylporphyrin has been reported for the first time.[112] Separation was carried out on a quartz capillary column (6 m × 0.3 mm) with Silicone OV-1 and a programmed temperature increase from 60 to 300 °C followed by exposure to an isothermal system. It was also possible to chromatograph porphyrin complexes of zinc, palladium-(II), titanyl, and platinum(II) under similar conditions. Satisfactory results were obtained when a glass column (10 m × 0.3 mm) with CP Sil S as liquid phase was used. The separation of complexes of silicon, aluminium, gallium, rhodium(III), and nickel with octaethylporphyrin, etioporphyrin I, and etioporphyrin III under similar

conditions was subsequently reported.[113] Metalloporphyrin complexes are the least volatile of all those used up to now in the chromatography of metal complexes with organic ligands, their separation was only achieved because of their excellent thermal stability and by using short capillary columns. It is probably true that because of the difficult quantitative conversion of metal ions to porphyrin complexes, at the present time the use of the latter for practical analysis cannot be considered.

VI. GAS CHROMATOGRAPHY OF METAL β-DIKETONATES IN LIQUID VAPOUR

The studies initiated in 1971 by Fujinaga et al.[114] on the chromatography of metal β-diketonates using a carrier gas with vapour from the corresponding β-diketone added (this method is usually not quite correctly called gas chromatography in ligand vapour—GCLV) have undergone further development. Thus, the determination by GCLV of trace amounts of beryllium as its trifluoroacetylacetonate in aluminium and its alloys with magnesium has been reported.[43] Analysis was carried out on a glass column (90 × 0.3 cm) filled with 0.5% Silicone SE-30 on glass beads at 130 °C. The carrier gas was argon with 0.05% TFA added, and a plasma detector with electrodeless discharge was used. The detection limit reached 1×10^{-12} g of beryllium. A similar method[115] was used to determine traces of copper and aluminium in metallic zinc.

A short communication[116] reports for the first time the complete separation of trifluoroacetylacetonates of four neighbouring rare earth elements (gadolinium, terbium, dysprosium, and holmium) on a column with a mixture of 0.2% PEG-20 M and 1.8% Silicone OV-17 on Chromosorb W at 240 °C. The gas carrier was helium with an extremely high concentration (10%) of TFA vapour, and a katharometer detector was used. Unfortunately, the column length was not stated in the study.

The separation of hexafluoroacetylacetonate adducts of rare earth radionuclides with TBP and TOPO on a column (2 m × 2.4 mm) with 2% polyphenyl ether or 3% Dexsil-300 on Chromosorb W has also been reported.[117] The carrier gas was saturated with HFA vapour at 60 °C. The column temperature was programmed to increase from 150 to 215 °C (8 K/min). A chromatogram which indicates the satisfactory separation of ten rare earth adducts over a period of 8 minutes was shown in the study.

The chromatographic behaviour of nickel and a number of other metal chelates with TFA under GCLV conditions has been studied[118] and a method for determining nickel in steel has been reported. Lead, cadmium, tellurium, molybdenum, and tungsten interfered with the determination. The determination of palladium as its trifluoroacetonylacetonate in the other metals of the platinum group using GCLV has been reported.[119] Other studies[27,120–122] have also been devoted to the application of GCLV.

When a chelate of europium with PTA was chromatographed in carrier gas containing acetylacetone vapour, ligand exchange occurred and less volatile mixed chelates were formed, containing PTA and AA anions.[27] A similar phemenon was found when an adduct of europium β-diketonate with TBP was chromatographed. When ligand vapour (HFA) was introduced into the carrier gas (1.6×10^{-6} g/ml) it was possible to obtain symmetrical peaks of hexafluoroacetylacetonate adducts of americium, curium, europium, terbium, and lutetium with TBP on a column with 5% Silicone SE-30 on Chromatone N AW DMCS at 205 °C.[122] The detection limits reached 5×10^{-8} g for americium and 3×10^{-9} g for curium.

The separate determination of manganese(II) and (III) ions in aqueous solution as chelates with TFA using GCLV has been reported.[123] One study[124] examines trifluoroacetylacetonates of chromium, aluminium, and iron by means of GCLV. Addition of TFA vapour to the carrier gas without exception improved the calibration curves of all the chelates, even that of the most stable chromium chelate.

VII. BEHAVIOUR OF METAL CHELATES ON A CHROMATOGRAPHY COLUMN

The abnormal effects that occur when the β-diketonates of many metals are chromatographed have been of interest to reseach workers for a long time. Among these effects are the irreversible adsorption of the first samples of chelate on a new column, the "memory" effect of a column, the "disappearance" of small samples of chelate on a column, the abnormal broadening of peaks, and so on. These phenomena have been described in detail in, for example, one monograph.[18] Berezkin[125] showed that such effects are the partial manifestations of general characteristics of the chromatographic process complicated by an appreciable degree of irreversible or quasi-irreversible chemisorptive interaction beween the components being separated and the column packing. In the case of metal complexes such as β-diketonates this type of interaction is likely to occur mainly with elimination of one ligand from the complex to give a free β-diketone molecule and is accompanied by attachment of the residue of complex to the matrix (solid support or liquid phase):

$$ML_n + HA \rightarrow ML_{n-1}A + HL$$

where M is metal, L is ligand, H is mobile hydrogen, A is matrix, and HL is free β-diketone.

This hypothesis, which was proposed some time ago,[18] was supported experimentally for the first time in one study,[126] where it was shown that rare earth dipivaloylmethanates were adsorbed on the column as cation complexes containing two ligand molecules.

The abormal effects mentioned above have been investigated in detail on copper(II) trifluoroacetylacetonate as a model.[127,128] A study of the distribution of copper chelate adsorbed on the column using a ^{64}Cu radioisotope showed that the adsorption depended on the quantity of chelate introduced, the content of the liquid phase, the nature of the solid support and the liquid phase, and the temperature. Considerable adsorption of chelate by wads of glass wool and fluoroplastic fibre holding the packing in the column was observed. The adsorption of chelate in the column was partly reversible.

More recently a similar study was published, being devoted to the chromatographic behaviour of zinc di(trifluoroethyl)dithiocarbamate[129] on a column, and it was carried out using a ^{65}Zn radioisotope. The authors also observed considerable adsorption of chelate on glass, quartz, and Teflon wool and indicated that the best results were obtained using metal gauze as wadding. To reduce the adsorption effects it was recommended to use glass and quartz capillarly columns rather than packed columns.

The interaction processes between metal β-diketonates and packing and with each other that occur on a column when the chelates of two different metals are chromatographed was studied by computer simulation.[130] The abnormal effects due to adsorption of hexafluoroacetylacetonate adducts of americium, curium, and some rare earth elements have also been described.[122]

Similar abnormal effects occurred when copper and iron β-diketonates were chromatographed on quartz capillary columns with different liquid phases. The partial oxidation of vanadium(III) chelate on a column to form vanadyl chelate was also observed. It is interesting to note that when nitrogen carrier gas was replaced by hydrogen the decomposition of the chelates in the column increased. Another study[132] is also devoted to the abnormal behaviour of metal β-diketonates on chromatographic columns.

VIII. GAS CHROMATOGRAPHIC DETERMINATION OF TRACE METALS

It is evident from what has been stated that the previous period of 11 years has been marked by considerable progress in the use of gas chromatography for practical analysis of trace amounts of metals. It is true that the limiting sensitivity of the method has not improved very much—the detection limit of most metals lies in the region of $10^{-11}-10^{-13}$ g per sample—and this is due to the absence of any noticeable improvement in the sensitivity of chromatographic detection in general. However, the total number of elements that can be determined with high sensitivity has increased substantially as a result of using new volatile complexes and the application of capillary columns.

A general Table featuring the present potentialities of gas chromatography in this field is given below.

Detection limits (m) of metals as volatile complexes using gas chromatography.

Metal	$m.10^{10}$.g	Refs.	Metal	$m.10^{10}$.g	Refs.
Be	0.0004	[133]	Ru	0.0024	[52]
Al	0.009	[134]	Rh	0.01**	[73]
Sc	0.03*	[135]	Pd	0.005**	[73]
V	0.085*	[135]	Ir	0.04**	[73]
Cr	0.00001	[34]	Pt	0.005**	[73]
Mn	500	[131]	Au	0.05**	[73]
Fe	0.13*	[135]	rare earths	200—300	[138]
Co	0.1	[136]	Cd	40	[63]
Ni	0.007	[137]	Tl	100	[105]
Cu	0.001	[137]	Pb	60	[63]
Zn	30	[63]	Hg	30	[63]
Ga	0.027*	[135]			

*Sensitivity of detection, $m'.10^{10}$ g/sec.

**Calculated on the basis of limiting dilution given in study.

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The η^5-Indenyl and η^5-Fluorenyl Complexes of Transition Metals and Their Comparison with the η^5-Cyclopentadienyl Compounds

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Data on the synthesis, structure, and reactivity of the η^5-indenyl and η^5-fluorenyl complexes of transition metals are examined and discussed. A comparison with the η^5-cyclopentadienyl analogues is made.
The bibliography includes 187 references.

CONTENTS

I. Introduction 967
II. Methods of synthesis and properties of the η^5-indenyl and η^5-fluorenyl complexes of transition metals 967
III. Conclusion 977

I. INTRODUCTION

The first η^5-indenyl complex (di-indenyliron)[1] was obtained almost simultaneously with ferrocene,[2] while difluorenylzirconium dichloride—the first compound with the η^5-fluorenyl ligand—was synthesised in 1965.[3] Nevertheless the chemistry of the indenyl and fluorenyl complexes of transitional metals has so far been little investigated, in contrast to the cyclopentadienyl complexes. However, the presence of a five-membered ring coordinated to the metal and of non-coordinated six-membered rings in the η^5-indenyl and η^5-fluorenyl complexes makes them of interest for the study of the influence of coordination to the metal on the distribution of π-electron density throughout the condensed system of the ligand. Indene and fluorene complexes are of interest also because different types of coordination to the transition metal (η^6, η^5, η^3, and η^1) are possible in such compounds and metallotropic rearrangments, widely investigated at the present time, are therefore characteristic of them. The η^5-indenyl and η^5-fluorenyl complexes of transition metals are more reactive than their cyclo-pentadienyl analogues in ligand exchange reactions because of their tendency to metallotropic rearrangements. The ease of ligand exchange in these complexes can be used in the synthesis of new organometallic compounds and also of catalysts of certain chemical processes.

II. METHODS OF SYNTHESIS AND PROPERTIES OF THE η^5-INDENYL AND η^5-FLUORENYL COMPLEXES OF TRANSITION METALS

1. Methods of Synthesis

The methods of synthesis of the η^5-indenyl and η^5-fluorenyl complexes of transition metals are usually analogous, with slight modifications, to those used in the synthesis of the η^5-cyclopentadienyl derivatives. The differences in the methods concern the reaction temperature and time, which is frequently associated with the lower stability of the η^5-indenyl and η^5-fluorenyl compounds.

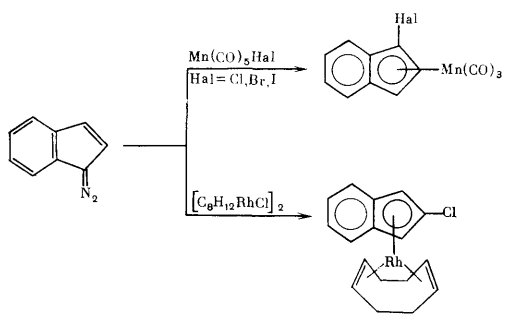
The commonest method of synthesis of these compounds involves the interaction of indenyl and fluorenyl derivatives of alkali metals, more rarely organotin compounds or Grignard reagents, with transition metal salts, carbonyls, or halogen-containing complexes:[3-44]

$$3C_9H_7K + MCl_4 \rightarrow (C_9H_7)_3MCl + 3KCl,\ M = U,\ Th;$$
$$C_9H_7K + W(CO)_6 \rightarrow [C_9H_7W(CO)_3]^{\ominus}K^{\oplus} + 3CO;$$
$$C_{13}H_9Li + [CrCl(NO)(CO)_2] \rightarrow C_{13}H_9Cr(CO)_2NO + LiCl.$$

In order to obtain mixed indenyl sandwich compounds, the transition metal salt is acted upon by alkali metal derivatives of indene and a second ligand:[45-47]

$$TiCl_4 + C_9H_7Na + C_8H_8K_2 \rightarrow C_9H_7TiC_8H_8.$$

A novel method of synthesis of the η^5-indenyl complexes with a halogen substituent in the π-ligand is based on the interaction of diazoindene with halogen-containing transition metal derivatives:[48,49]



One of the most general methods of synthesis of new compounds in organo-metallic chemistry involves the exchange of the carbonyl or halogen groups in metal complexes for *n*- and π-donor ligands (phosphines, olefins, acetylenes, etc.). This method is used widely also for the synthesis of η^5-indenyl and η^5-fluorenyl complexes which have not been described hitherto:[35,38,50-76]:

$$C_9H_7W(CO)_3(CH_3) + C_2H_4 \rightarrow C_9H_7W(CO)_2(CH_3)(C_2H_4) + CO,$$
$$(C_{13}H_9)_2MCl_2 + Na(S_2CNR_2) \rightarrow (C_{13}H_9)_2M(S_2CNR_2)Cl + NaCl,$$
$$M = Ti,\ Zr;\ R = CH_3,\ C_2H_5,\ iso\text{-}C_3H_7.$$

Polymetallic heteronuclear clusters containing the η^5-indenyl ligand have been obtained from the highly reactive η^5-indenylrhodium complexes.[77–83]

2. The Nature of the Metal–π–ligand Bond in the η^5-Indenyl and η^5-Fluorenyl Complexes. The Stability of the Complexes

In the study of the properties of the η^5-indenyl and η^5-fluorenyl complexes of transition metals, it has been frequently noted that these complexes are less stable than their η-cyclopentadienyl analogues.[26,27,32,84–86] According to modern ideas, the π electrons of the ligand are mainly involved in the bond between the π-ligand and the metal.[87] Consequently, the strength of the metal–π-ligand bond should be influenced by substituents in the π-ligand which alter its π-electron density. Theoretical calculations[88] for the indenyl and fluorenyl anions (in alkali metal salts) have shown that the six-membered aromatic rings participate, together with the five-membered ring, in the distribution of π-electron density (including the negative charge) in these anions. Presumably, in the η^5-indenyl and η^5-fluorenyl complexes of transition metals, in which only the five-membered ring is linked directly to the metal, there is also interaction of the π-electron clouds of the six- and five-membered rings, which can weaken the donor–acceptor interaction between the five-membered ring and the transition metal. Indeed, the study of titanium and zirconium complexes has shown that the strength of the metal–π-ligand bond is sensitive to the donor and acceptor characteristics of the substituents in the π-ligand. Thus the resistance of compounds of the type L_2MCl_2 (M = Ti or Zr; L = $C_5H_4CH_3$, C_9H_7, or C_9H_{11}) to decomposition and hydrolysis is correlated with the nature of the substituents in the five-membered ring: the η^5-indenyl derivatives are less stable while the η^5-tetrahydroindenyl derivatives are more stable than the unsubstituted η^5-cyclopentadienyl analogue. This has been attributed[84] to the fact that the six-membered ring in the η^5-indenyl complexes behaves as an electron-accepting substituent in relation to the five-membered ring bound to the metal, which leads to a lower stability of these compounds in polar organic solvents. On the other hand, the saturated cyclohexane ring, which is an electron-donating substituent, increases the stability of the η^5-tetrahydroindenyl complexes of titanium and zirconium. A lower stability of the indenyl complexes compared with the cyclopentadienyl complexes has been established for compounds of Group VII metals. Thus the interaction of η^5-$C_9H_7Re(CO)_3$ with nitrogen-containing bases (pyridine or urotropine) entails the cleavage of the metal–π-ligand bond and the formation of dinuclear complexes with bridging hydroxy- or alkoxy-groups.[89] On the other hand, the reactions of η^5-$C_5H_5Re(CO)_3$ with these bases lead only to substitution of the CO group by the *n*-donor ligand.[90]

Further weakening of the bond between the π-ligand and the metal in the η^5-fluorenyl complexes compared with the indenyl complexes is due to the increase in the number of benzene rings condensed with the five-membered ring, such rings withdrawing the π-electron density from the cyclopentadienyl ring. Indeed, difluorenyl derivatives have not been obtained for metals of the iron triad, which form the most stable dicyclopentadienyl complexes.[32]

Calculations of the force constants for the C≡O bonds in the complexes $C_5H_5Mn(CO)_3$, $C_9H_7Mn(CO)_3$, and $C_{13}H_9Mn(CO)_3$ [26] failed to indicate appreciable changes in these quantities on passing from η^5-$C_5H_5Mn(CO)_3$ to η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_{13}H_9Mn(CO)_3$, which indicates the retention of the same effective charge on the metal atom in all three complexes. The authors suggested that the decrease in the strength of the bond between the five-membered ring and the metal after its successive condensation with benzene rings is a consequence of the weakening of both donor–acceptor and dative metal–ring bonds.

A comparative quantitative estimate of the strength of the π-ligand–metal bond in the indenyl, fluorenyl, and cyclopentadienyl complexes was first made in relation to the carbonyl derivatives $LM(CO)_3$ (M = Mn or Re; L = η^5-C_5H_5, η^5-C_9H_7, or η^5-$C_{13}H_9$) or Group VII metals.[91] The authors used mass spectrometry for this purpose, which makes it possible to study the compounds with exclusion of the influence of the medium. The ratio of the sum of the intensities of the metal-containing ions (after subtracting the intensity of the metal ion) I_1 to the sum of the intensities of all the hydrocarbon ions and the metal ion I_2 was adopted as the measure of the strength of the metal–π-ligand bond. According to the results obtained by this method (see Table), the strength of the binding of the metal to the π-ligand diminishes greatly on passing from rhenium to manganese and diminishes appreciably in the sequence η^5-cyclopentadienyl > η^5-indenyl > η^5-fluorenyl complexes.

Mass-spectrometric data for the metal–π-ligand bond strengths.

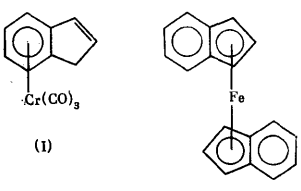
Compound	I_1/I_2	Compound	I_1/I_2
$C_9H_5Re(CO)_3$	87	$C_5H_5Mn(CO)_3$	1.9
$C_9H_7Re(CO)_3$	64	$C_9H_7Mn(CO)_3$	0.51
		$C_{13}H_9Mn(CO)_3$	0.34

3. The Structure of the η^5-Indenyl and η^5-Fluorenyl Complexes of Transition Metals

Three types of coordination are known for the π-complexes of indene and fluorene with transition metals: η^6-coordination [as in the complex (I)], η^5-coordination [as in the complex (II)], and η^3-coordination [as in the complex (III)]. A compound of type (I) belongs to the class of π-arene complexes and the η^5- and η^3-indenyl derivatives are analogues of the cyclopentadienyl and allyl complexes respectively. However, for the indenyl and fluorenyl complexes there apparently exists also a transitional type of coordination between η^5- and η^3-coordinations, for example, in the π-complexes of the lanthanides and the actinides.

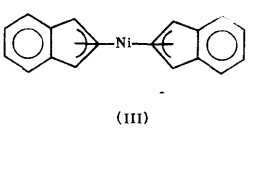
In the present review, we shall consider only η^5-coordination complexes and shall compare them with their cyclopentadienyl analogues.

The structure of the η^5-indenyl and η^5-fluorenyl complexes has been studied by IR spectroscopy,[68,92–94] mass spectrometry,[95] NMR spectroscopy,[96–100] and X-ray diffraction analysis (XDA).[27,57,59,101–102]



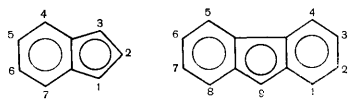
(I)

(II)



(III)

Important information about the type of coordination of the π-ligand in transition metal complexes can be obtained from study of the ^1H and ^{13}C NMR spectra. This is due to the fact that the proton and ^{13}C signals in the NMR spectra of the organic fragments π-coordinated to the metal undergo an appreciable upfield shift compared with the non-coordinated organic compound. Indeed, in the chromium(I) complex with η^6-coordinated indene, all the signals of the carbon atom nuclei in the six-membered ring undergo a 30 p.p.m. upfield shift, while the signals of the non-bridging carbon atoms in the five-membered ring hardly change compared with the non-coordinated indene.[97] On the other hand, in the case of the di-η^5-indenyl complex of iron(II), there is an appreciable upfield shift of the carbon atom signals of the five-membered rings, including bridging carbon atoms, while the signals of the other four carbon atoms in the six-membered rings remain in the same range as for the non-coordinated indene.[97] In the ^{13}C NMR spectrum of the nickel(III) complex in which the π-ligand is η^3-coordinated to the metal atom, only the signals due to the carbon atoms in the 1-, 2-, and 3-positions are appreciably displaced, the signal of the nucleus of the C(3) atom being displaced downfield and those of the nuclei of the C(1) and C(2) atoms being displaced upfield compared with free indene.[97] Here and henceforth the following numbering of the atoms is used:



It is believed[99] that the chemical shifts of the quaternary bridging carbon atoms of the indenyl ligand in the ^{13}C NMR spectra are a good indicator for the determination of the η^5- or η^3-coordination of the π-ligand. Thus the relatively small chemical shifts of the bridging carbon atoms in the dimer $[C_9H_7Mo(CO)_2]_2$ (111.5 p.p.m.) agree with the XDA data indicating the η^5-coordination of the indenyl ligands.

Valuable information about the distortion of the η^5-coordination of the indenyl and fluorenyl ligands has been obtained from ^1H and ^{13}C NMR spectra. Thus a slight distortion of the η^5-type of coordination towards η^3-binding was manifested in the ^1H NMR spectrum of the compound $C_9H_7Rh(C_2H_4)_2$.[19] Only the proton signal in the 2-position in the π-indenyl ligand was split as a result of the interaction with the ^{103}Rh nucleus of the kind observed for the η^3-allyl complexes of rhodium. However, signals of all the carbon atoms of the five-membered ring of this complex appear as doublets in the ^{13}C NMR spectrum as a consequence of the interaction of the ^{13}C nuclei with the ^{103}Rh atoms, which indicates the binding of the rhodium atom to all five carbon atoms.[19] An analogous distortion of the η^5-coordination was reflected in the ^1H and ^{13}C NMR spectra of the complex $C_9H_7Co[P(OR)_3]_2$.[17]

Judging from the NMR spectra, there is some contribution of η^1-type coordination in the fluorenyl complex η^5-$C_{13}H_9Co[P(OR)_3]_2$: the signal of the proton in the 9-position of the π-ligand is at stronger field than for the complexes η^5-$C_{13}H_9Mn(CO)_2L$ (L = CO or PPh_3) and $(\eta^5$-$C_{13}H_9)Zr(\eta^3$-$C_{13}H_9)Cl_2$. Furthermore, the spin–spin coupling constant (SSCC) of the carbon nucleus in the 9-position in the π-ligand to the phosphorus nucleus in phosphite is manifested in the ^{13}C NMR spectrum of the cobalt complex.[17]

The most complete idea about the structure of the η^5-indenyl and η^5-fluorenyl complexes of transition metals is provided by XDA. The first X-ray diffraction studies on η^5-indenyl complexes were performed at the end of the 1950's. The XDA data for di-indenyliron[101] indicated a great similarity between its structure and that of ferrocene. In the planar indenyl ligand, the C–C bond lengths are equalised (1.43 Å) and the C–C–C angles are 120 ° in the six-membered ring and 108° in the five-membered ring, which corresponds to a fully conjugated aromatic system. Di-indenylruthenium has an analogous structure.[102] Subsequently, in the study of the structure of the η^5-indenyl complexes, it was established that they have a number of characteristic features distinguishing them from their η^5-cyclopentadienyl analogues. A slight departure from planarity of the π-ligand as well as a difference in the metal–carbon bond lengths has been observed for the η^5-indenyl complexes: the length of the bonds between the metal and the bridging carbon atoms is somewhat greater than that of the bonds with the remaining three atoms. Thus there is a slight distortion of the η^5-coordination of the indenyl ligand to the metal in the direction of η^3-binding.[57,59,103–105] The mechanism of this distortion involves the movement of the metal atom parallel to the plane of the indenyl ligand. In recent years, the "slip parameter" Δ has been used to estimate this effect.[107–109] The parameter Δ represents the length of the vector between the centre of the five-membered ring and the projection of the metal atom onto the plane of the ring. For η^5-indenyl complexes, the "slip parameter" is usually $\Delta < 0.3$.[107] All the characteristic features of the indenyl complexes have been observed in a study of the structure of bis(1,3-dimethylindenyl)iron hexafluorophosphate: the distortion from planarity of the π-ligand was 0.049 Å and the difference between the Fe–C (five-membered ring) bond lengths was 0.08 Å.[103]

Comparison of the structures of the Group IVB metal complexes $(C_9H_7)_2M(CH_3)_2$ (M = Ti, Zr, or Hf) showed that the difference between the metal–carbon (five-membered ring) bond lengths depends on the nature of the metal: it is 0.19 Å for the titanium compound, 0.12 Å for the zirconium compound, and 0.13 Å for the hafnium compound.[111]

Undistorted η^5-coordination of the indenyl ligand has been observed only in exceptional cases. Such an example is provided by the complex $(CO)(\eta^5$-$C_9H_7)Mo \equiv Mo(C_9H_7$-$\eta^5)(CO)$.[112] The indenyl ligands in this complex are planar and their five-membered rings are linked almost symmetrically to the molybdenum atoms: the difference between the Mo–C(C_5H_3) bond lengths is only 0.06 Å.[112]

A rare example of structural comparison of analogous η^5-indenyl, η^5-fluorenyl, and η^5-cyclopentadienyl complexes has been described.[27,113] For $C_9H_7Cr(CO)_2NO$, $C_{13}H_9Cr(CO)_2NO$, and $C_5H_5Cr(CO)_2NO$, which have in the main similar structures, an increase has been observed in the distance between the chromium atom and the centre of the five-membered ring in the following series of complexes: η^5-cyclopentadienyl, η^5-indenyl, η^5-fluorenyl (1.845, 1.866, and 1.884 Å respectively), and also a decrease in the Cr–N bond lengths with the simultaneous increase in the Cr–CO distances for the indenyl and fluorenyl complexes.

Complexes where the fluorenyl and indenyl ligands are involved in different types of coordination to the same metal atom are of special interest: $(\eta^5$-$C_9H_7)W(\eta^3$-$C_9H_7)(CO)_2$,[114] $(\eta^5$-$C_9H_7)V(\eta^3$-$C_9H_7)$. $.(CO)_2$,[109] and $(\eta^5$-$C_{13}H_9)Zr(\eta^3$-$C_3H_9)Cl_2$.[115,116] In the tungsten complex, one of the indenyl ligands is linked to the metal atom almost symmetrically, the W–C (five-membered ring) bond lengths oscillating from 2.27 to 2.37 Å but remaining within the limits usual

for Group IVB metal complexes. This ligand is planar overall, the C–C bond lengths [1.41(3) Å] indicating the delocalisation of the π-electrons over the aromatic system. For the second indenyl ligand, the W–C (five-membered ring) bond lengths are 3.22(2) and 3.12(2) Å for the bridging carbon atoms and 2.26(2), 2.46(2), and 2.44(2) Å for the non-bridging atoms. This indenyl ligand has lost its planarity as a consequence of η^3-coordination: its five-membered ring is bent at an angle of 26°. For the vanadium complex, large differences between the η^5- and η^3-indenyl ligands have also been observed. For the η^5-coordinated ligand, the V–C (five-membered ring) bond length varies from 2.261(3) to 2.388(3) Å and the "slip parameter" Δ is 0.17. In the η^3-indenyl ligand, the dihedral angle between the planes of the η^3-allyl fragment and the six-membered ring is 12.0(3)°. The V–C (five-membered ring) bond lengths are 2.379, 2.184, and 2.359 Å for the carbon atoms of the allyl fragment and 2.857 and 2.876 Å for the bridging carbon atoms; Δ = 0.56.[109]

The zirconium complex $(\eta^5\text{-}C_{13}H_9)Zr(\eta^3\text{-}C_{13}H_9)Cl_2$ is one of the few compounds with fluorenyl ligands bound in different ways. The difference between the coordinations of the fluorenyl ligands in this complex follows from a comparison of the average Zr–C (five-membered ring) bond lengths. For one of these ligands, the bond length 2.56(7) Å is comparable to the bond length found for $(\pi\text{-}C_5H_5)_2Zr.Cl_2$, while for the other the average value of this distance is 2.52(8) Å for the three non-bridging carbon atoms and 2.80(1) Å (absence of a bond) for the two bridging atoms.[115,116] The authors believe that fundamental geometry of the molecule and the type of bond between zirconium and the π-ligands are determined by the steric requirements imposed by the bulky fluorenyl groups.

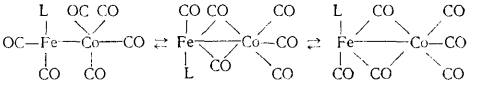
In the π-indenyl complexes of the lanthanides and actinides, distortion in η^5-coordination to the metal atom reaches a higher level than in the complexes of other transition metals. On the other hand, the changes in the bond length and in the planarity of the indenyl ligand in these complexes are smaller than for the η^3-coordinated indenyl ligand. As a result of this, some workers classify the indenyl complexes of the lanthanides and the actinides as η^5-derivatives, while others regard them as η^3-derivatives. XDA has been carried out for a series of samarium,[117] thorium,[118] and uranium[119–122] compounds. Having to choose betweeen the η^5- or the η^3-coordination of the indneyl ligand in $[1,4,7\text{-}(CH_3)_3C_9H_4]_3UCl$, Goffart et al.[120] decided on the η^5-type of binding on the basis of not only XDA data but also on the basis of a qualitative comparison of magnetic susceptibilities, vibrational spectra, and ^1H NMR spectra of this compound and its cyclopentadienyl analogue. The U–C (five-membered ring) bond lengths are 2.91 Å for the bridging carbon atoms and 2.72 Å for the non-bridging atoms. In the analogous thorium complex $[1,4,7\text{-}(CH_3)_3C_9H_4]_3.ThCl$, the Th–C (five-membered ring) bond lengths vary from 2.721(3) to 2.845(4) Å for the non-bridging carbon atoms and from 2.931(3) to 2.946(3) Å for the bridging carbon atoms. However, the authors[118] believe on the basis of these data that the indenyl ligands in the thorium complex are η^3-bound and that there is only a very weak interaction between the metal and the bridging carbon atoms in the five-membered rings.

Thus X-ray diffraction studies on the η^5-indenyl and η^5-fluorenyl complexes and the analogous η^5-cyclopentadienyl complexes have shown that the molecular structures of these compounds are in many respects similar: the η^5-coordinated ligand is planar with equalised C–C bonds, while in the carbonyl derivatives the metal–CO and C–O bond lengths are comparable. However, in contrast to the η^5-cyclopentadienyl complexes, in the η^5-indenyl and η^5-fluorenyl derivatives the bond lengths between the metal and the carbon atoms of the five-membered ring are different: for the three-non-bridging carbon atoms in the η^5-C_9H_7 ligand the metal–carbon bond lengths are smaller compared with the two bridge bonds. Some breakdown of the planarity of the η^5-indenyl and η^5-fluorenyl ligands is observed.

4. Stereochemical Non-Rigidity of the η^5-Indenyl Complexes

Comparison of analogous η^5-indenyl and η^5-cyclopentadienyl complexes of transition metals makes it possible to elucidate the influence of the η-ligand on the physicochemical properties and reactivity, in particular, on the properties of the other ligands. The nature of the π-ligand influences the dynamic equilibrium of isomers and conformers in solutions and barriers to the rotation of ethylene and acetylene ligands.

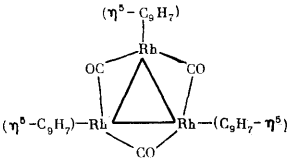
The IR spectra of the complexes $\pi\text{-}LFe(CO)_2Co(CO)_4$ (L = C_5H_5, $CH_3C_5H_4$, or C_9H_7), established that these compounds exist in solutions in the form of equilibrium mixtures of two isomers containing bridging CO groups [the isomers (B) and (C)] and one isomer having only terminal CO ligands [the isomer (A)]:



(A) (B) (C)

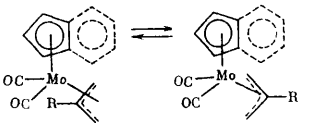
The fraction of the isomer (A) diminishes with decrease in temperature, with increase in solvent polarity, and in the sequence of ligands $\eta^5\text{-}C_9H_7 > \eta^5\text{-}CH_3C_5H_4 > \eta^5\text{-}C_5H_5$.[123] According to XDA data, in the solid state the complex $\eta^5\text{-}C_9H_7Fe(CO)_2Co(CO)_4$ has the structure (B).[124]

An analogous CO group migration process has been investigated for the η^5-indenyl cluster (IV). It was observed that the indenyl cluster exists in the form of only one isomer with bridging CO groups and that the ^{13}C NMR spectrum does not exhibit a temperature dependence in the carbonyl region, in contrast to its η^5-cyclopentadienyl analogue:[59]



(IV)

A series of studies have been devoted to the investigation of the stereochemistry of a number of η^5-indenyl and η^5-cyclopentadienyl complexes of molybdenum[125–127] and iron[128,129] by ^1H NMR. It was established in this way that in solution the compounds $\eta^5\text{-}LMo(CO)_2(\pi\text{-}C_3H_4R)$ (L = $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7$) exist as a mixture of two forms (D) and (E):[126]



(D) (E)

For the η^5-indenyl derivatives of molybdenum with R = CH_3, Cl, or Br, the equilibrium is displaced to the left, while in the case of the

η^5-cyclopentadienyl complexes the substitution of the hydrogen atoms at the central carbon atom in the π-allyl group shifts the equilibrium to the right.[126] The analogous iron and ruthenium compounds η^5-LM(CO)(π-C_3H_4R) (M = Fe or Ru; L = C_5H_5 or C_9H_7) have been isolated in the form of only one isomer (E).[128]

In the study of the temperature variation of the ^1H NMR spectra of the rhodium complexes $LRh(C_2H_4)_2$ (L = η^5-C_5H_5 or η^5-C_9H_7), an appreciable influence of the π-ligand on the barrier to the rotation of ethylene was observed.[19,130] The barrier to the rotation of the ethylene ligand in the η^5-indenyl compound (10.5 ± 0.4 kcal mol^{-1}) is much lower than in the η^5-cyclopentadienyl compound (15.0 ± 0.2 kcal mol^{-1}). The coalescence temperature is −90° for the former complex and −19° for the latter.[19] The authors[19] draw a parallel between the lower barrier to the rotation of the olefin in the η^5-indenyl complex and the greater ease of the substitution of the C_2H_4 group in the same compound compared with η^5-$C_5H_5Rh.(C_2H_4)_2$.

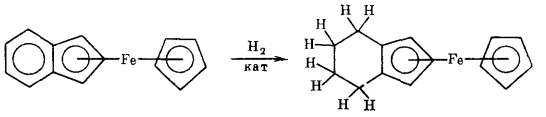
In the cationic complexes of molybdenum with dimethylacetylene of the type $LMo[P(OCH_3)_3]_2(CH_3C{\equiv}CCH_3)^+BF_4^-$ (L = η^5-C_5H_5 or η^5-C_9H_7), the influence of the π-ligand on the barrier to the rotation of acetylene has also been observed: the coalescence temperature is −40° for the indenyl complex and below −90° for the cyclopentadienyl complex.[50]

However, the influence of the indenyl ligand is not always manifested. For example, although the ^1H NMR spectra of the ethylene and acetylene complexes of tungsten $LW(CO)_2(CH_3)(C_2H_4)$ and $LW(CO)(CH_3)(CH{\equiv}CR)$ (L = η^5-C_5H_5 or η^5-C_9H_7; R = H or CH_3) do in fact exhibit a temperature dependence, apparently associated with the hindrance of rotation of the π-olefin and π-acetylene ligands, about the metal−ligand bond, the barriers to rotation of the η^5-cyclopentadienyl and η^5-indenyl compounds are approximately equal.[35,52,53,131] In contrast to the tungsten compounds, in the cationic iron complexes $[LFe(CO)_2(C_2H_4)]^+BF_4^-$ (L = η^5-C_5H_5 or η^5-C_9H_7) there is free rotation of the ethylene group regardless of the nature of the π-ligand.[129]

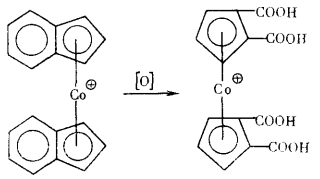
In certain studies, the barriers to rotation of the η^5-indenyl and η^5-cyclopentadienyl ligands have been compared qualitatively in analogous complexes. Thus in the π-allyl complexes of molybdenum η^5-$LMo(CO)_2$(π-C_3H_4R) (L = C_5H_5 or C_9H_7), the η^5-coordinated ligand rotates freely about the Mo−L bond, but the barrier to rotation of the indenyl ligand is higher than for the cyclopentadienyl ligand. As a result, there exists a preferred conformation of the indenyl complexes in which the six-membered ring is arranged above the π-allyl ligand.[126] The hindered rotation of the π-indenyl ligand has also been observed for the dinuclear complex η^5-$C_9H_7Rh.(CO)_3Cr(CO)[(CH_3)_2C_6H_3]$ in a study of the temperature variation of the ^{13}C NMR spectra.[132]

5. Chemical Shifts

(a) *The reduction and oxidation of the η^5-indenyl complexes.* Hydrogenation with hydrogen in the presence of catalysts (Adams catalyst, platinum dioxide, etc.) has been investigated for a series of indenyl complexes such as di-indenyliron,[133] di-indenylruthenium,[16] cyclopentadienyl(indenyl)iron,[46] ethylenedi-indenyltitanium dichloride,[9,25] di-indenyltitanium dichloride,[32] di-indenylzirconium dichloride,[32] and the dimer of dicarbonylindenyliron.[134] It was found that in all cases only the double bonds of the six-membered rings of the π-ligand are hydrogenated, which apparently indicates the olefinic nature of these bonds:



In contrast to the indenyl complexes, the hydrogenation of the six-membered rings of the fluorenyl ligands in $(\eta^5$-$C_{13}H_9)(\eta^3$-$C_{13}H_9)Zr.Cl_2$ could not be achieved.[32] An example of the oxidation of a six-membered ring, not coordinated to the metal, on treatment of a cationic cobalt complex with potassium permanganate is also known:[135]

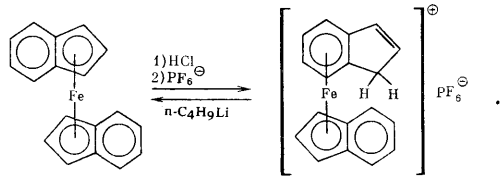


The oxidation-reduction processes in η^5-indenyl and η^5-fluorenyl complexes have also been investigated by electrochemical methods. The majority of these studies have shown that the condensed six-membered rings in the η^5-indenyl and η^5-fluorenyl ligands possess electron-accepting properties, diminishing the electron density on the metal. Thus the replacement of the η^5-cyclopentadienyl ligand by the η^5-indenyl ligand lowers appreciably the reduction potential of cobaltocenium salts: −1.16 V for $(\eta^5$-$C_5H_5)_2Co^+$ and −0.5 V for $(\eta^5$-$C_9H_7)_2Co^+$.[6] The same effect has been observed in the polarographic reduction of rhodium complexes with duroquinone: −1.76 and 2.03 V for $(\eta^5$-$C_5H_5)$Rh(duroquinone) and −1.43 and 1.76 V for $(\eta^5$-$C_9H_7)$Rh(duroquinone).[136] As a result of a study of the electrochemical oxidation of the 17-electron titanium complexes η^5-$LTi.(\eta^8$-$C_8H_8)$ (L = $CH_3C_5H_4$, C_5H_5, C_9H_7, or $C_{13}H_9$), the authors concluded that the influence of the six-membered condensed rings in these complexes is opposed to that of the CH_3 group.[137] However, data have been published on the electrochemical oxidation of iron compounds [0.49 V for $(\eta^5$-$C_5H_5)_2Fe$, 0.35 V for $(\eta^5$-$C_5H_5)$ $(\eta^5$-$C_9H_7)Fe$, and 0.21 V for $(\eta^5$-$C_9H_7)_2Fe$], from which it follows that the replacement of the η^5-cyclopentadienyl ligand by the η^5-indenyl ligand as well as the introduction of the electron-donating substituent into the π-ligand facilitates the oxidation of the central metal atom.[138]

(b) *Metallotropic rearrangements.* In the complexes of transition metals with polycyclic condensed aromatic ligands, the metal is capable of migrating from one ring to another under the influence of various reagents, altering thereby the character of the binding to the π-ligand. These metallotropic rearrangements are characteristic of the indenyl and fluorenyl complexes.

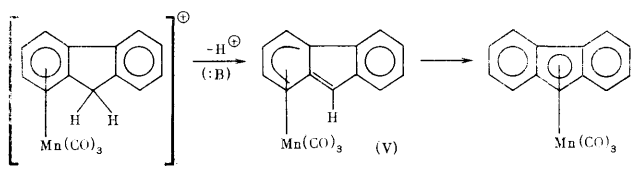
The first example of such inter-ring rearrangement was reported in 1971.[139] In a study of the interaction of di-indenyliron with boron trifluoride etherate, an analogous rearrangement was observed simultaneously.[140] In 1976, the protonation of di-indenyliron and cyclopentadienyl(indenyl)iron was investigated.[141] Under the influence of CF_3COOH and HCl, the iron atom migrated in the

η^5-indenyl complexes from the five-memberd ring to the six-membered ring and η^6-indene complexes of iron were obtained:

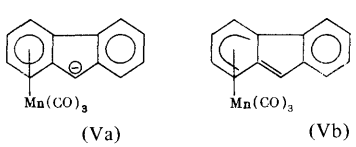


In order to elucidate the stereochemistry of the protonation reaction, the authors studied the interaction of $(\eta^5\text{-}C_9H_7)_2Fe$ with DCl and of $(\eta^5\text{-}1,1,3,3\text{-}C_9H_3D_4)_2Fe$ with HCl. Analysis of the ^1H NMR spectra of the products obtained in these reactions showed that the protonation is stereospecific. It has been suggested[141] that the iron atom is protonated initially and the hydrogen is then transferred to the five-membered ring so that *endo*-addition should result from such "ricochet reaction". Treatment of the η^6-indene complex with n-butyl-lithium regenerated $(\eta^5\text{-}C_9H_7)_2Fe$ in 23% yield. The study of the deprotonation of compounds partly labelled with deuterium and analysis of the mass spectra of the products obtained enabled the authors to conclude that the deprotonated reaction is non-stereospecific. Examples of metallotropic rearrangements of the π-complexes of other Group VIII metal atoms, for example rhodium and iridium, have also been described in the literature.[142-144]

The first metallotropic $\eta^6 \rightarrow \eta^5$-rearrangement of the π-complexes of Group VII metals was observed in a study of the deprotonation of tricarbonylfluorenemanganese:[145]



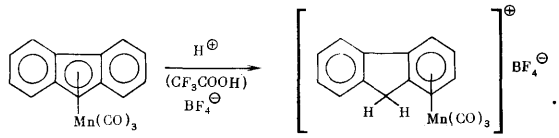
The complex $\eta^6\text{-}C_{13}H_9Mn(CO)_3$ (V) formed initially was converted on heating into the thermodynamically more stable $\eta^5\text{-}C_{13}H_9Mn.(CO)_3$. Two limiting structures were proposed initially for compound (V): the zwitter-ionic structure (Va) and the methylenecyclohexadienyl structure (Vb):[146]



(Va) (Vb)

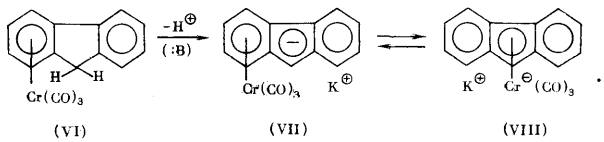
Subsequently XDA showed that the manganese complex (V) has the structure typical of cyclohexadienyl derivatives.[147] Theoretical calculations for the $\eta^6 \rightarrow \eta^5$ rearrangement of the fluorenyl complexes of manganese showed that the η^6-isomer is more stable than the η^5-isomer and that the activation energy for the rearrangement is 25 kcal mol^{-1}.[148] Subsequently kinetic studies on the $\eta^6 \rightarrow \eta^5$ rearrangements of three fluorenyl complexes of manganese, namely $\eta^6\text{-}C_{13}H_9Mn(CO)_3$, $\eta^6\text{-}C_{13}H_9Mn(CO)_2P(C_4H_9\text{-}n)_3$, and $\eta^6\text{-t-}C_4H_9.C_{13}H_8Mn(CO)_3$, confirmed these quantum-chemical calculations.[149] Since the activation energies for the $\eta^6 \rightarrow \eta^5$ rearrangements of $\eta^6\text{-}C_{13}H_9Mn(CO)_3$ and $\eta^6\text{-}C_{13}H_9Mn(CO)_2P(C_4H_9\text{-}n)_3$ proved to be similar and bearing in mind that the replacement of the CO group by the electron-donating phosphine ligand greatly increases the basicity of the central metal atom, the authors concluded that the basicity of the metal does not influence the rate of the rearrangement.

The reverse $\eta^5 \rightarrow \eta^6$ rearrangement was discovered in a study of the protonation of η^5-fluorenyltricarbonylmanganese with trifluoroacetic acid:[150]



In this case, the acid proton apparently adds directly to the fluorenyl ligand. In the η^5-indenyltricarbonylmanganese complexes of manganese and rhenium, the analogous $\eta^5 \rightarrow \eta^6$ rearrangement is observed only on treatment with stronger acids, namely $HFSO_3$ and $AlCl_3$.HCl, which is probably due to the lower basicity of the indenyl ligand compared with the fluorenyl ligand.[151] The increase in the basicity of the central metal atom in the complexes $\eta^5\text{-}C_9H_7.Mn(CO)_2PPh_3$, $\eta^5\text{-}C_9H_7Re(CO)_2PPh_3$, and $\eta^5\text{-}C_{13}H_9Mn(CO)_2PPh_3$ compared with the metal tricarbonyl leads to the protonation of the metal atom in the $CF_3COOH - CH_2Cl_2$ medium and there is no metallotropic rearrangement under these conditions.[151] On the other hand, it has been reported[149] that $\eta^5\text{-}C_{13}H_9Mn(CO)_2.P(C_4H_9\text{-}n)_3$ reacts rapidly with hydrogen chloride, affording the rearrangement product $[\eta^6\text{-}C_{13}H_{10}Mn(CO)_2P(C_4H_9\text{-}n)_3]^+X^-$ and the reaction is non-stereospecific. Hence the authors conclude that the acid proton adds directly to the carbon atom in a 9-position in the fluorenyl ligand.

The inter-ring metallotropic rearrangements of the indenyl and fluorenyl complexes of Group VIB transition metals have been widely investigated by Nesmeyanov's school. In relation to the fluoride anion coordinated to the $Cr(CO)_3$ group, Nesmeyanov and co-workers[152,153] observed the first instance of metallotropic tautomerism where both the initial complex and the product of its metallotropic rearrangement are in equilibrium. Treatment of $\eta^6\text{-}C_{13}H_{10}.Cr(CO)_3$ (VI) with an excess of potassium t-butoxide in tetrahydrofuran (THF) at −70 °C led to its complete conversion into $\eta^6\text{-}C_{13}H_9Cr(CO)_3^-K^+$ (VII), whose isomerisation to $\eta^5\text{-}C_{13}H_9Cr.(CO)_3^-K^+$ (VIII) was observed even at 0 °C and equilibrium was attained after 1 h at 25 °C:



(VI) (VII) (VIII)

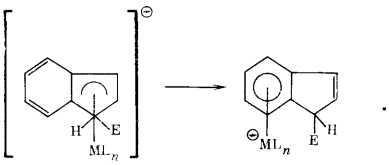
An equilibrium mixture of the same composition was obtained from the mercury derivative:

$$[\eta^5\text{-}C_{13}H_9Cr(CO)_3]_2Hg \xrightarrow{K/Na} (VIII) \rightleftarrows (VII).$$

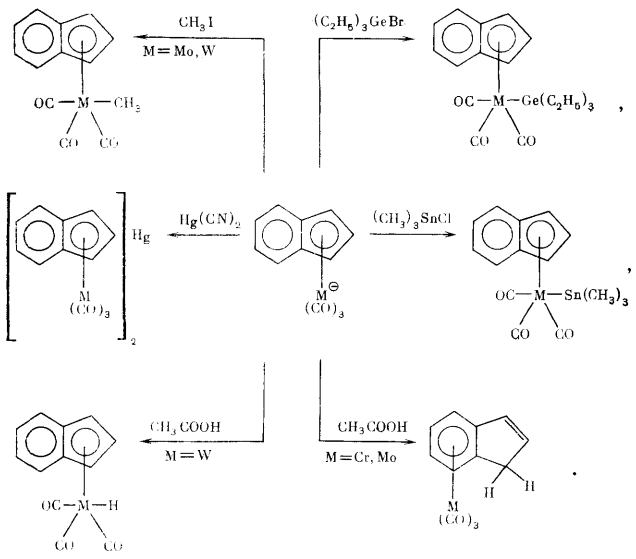
The kinetics of this equilibrium rearrangement have been studied by IR spectroscopy and also by ^1H and ^{13}C NMR.[152-156] The equilibrium constant was shown to depend on the nature of the cation, the solvent, and the concentration of the compound. It was also demonstrated that the rearrangement proceeds via an intramolecular mechanism.[157]

In contrast to η^6-fluorenechromium tricarbonyl, the deprotonation of η^6-fluorenemolybdenum tricarbonyl and η^6-indenechromium tricarbonyl leads to only one isomer of type VIII—$\eta^5\text{-}C_{13}H_9(CO)_3.Mo^-$ and $\eta^5\text{-}C_9H_7(CO)_3Cr^-$ respectively.[33,158]

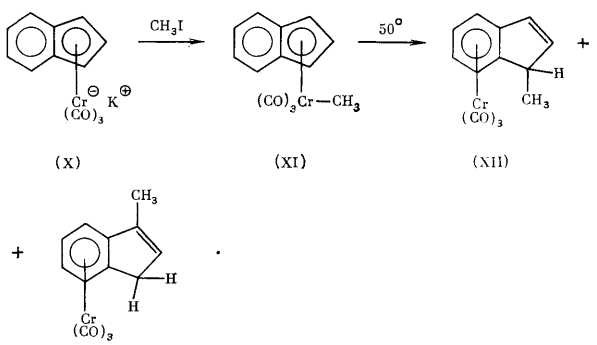
The study of the reactions of the η^5-indenyl and η^5-fluorenyl anionic complexes of Group VIB metals with electrophiles demonstrated a difference between these derivatives and their η^5-cyclopentadienyl analogues. This is associated primarily with the fact that, in contrast to the η^5-cyclopentadienyl systems, the polycyclic systems have an additional pathway leading to the stabilisation of the intermediate (IX)—as a result of the shift of the organometallic group to the six-membered ring of the π-ligand. This process may be thermodynamically preferable to the dissociation of the C—H and C—E bonds:[159]



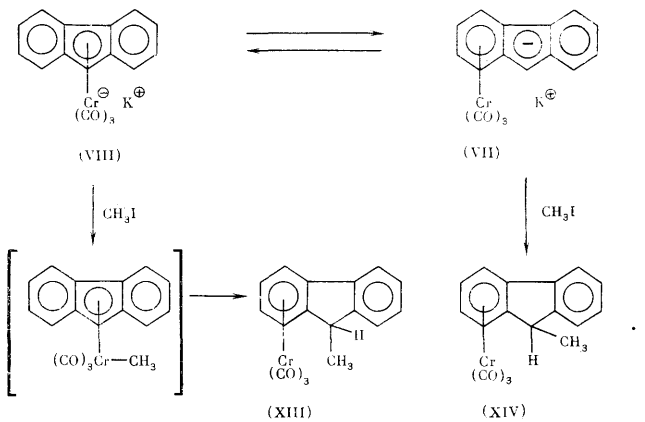
The nature of the metal and the reagent influence appreciably the direction of the reactions of anionic η^5-indenyl complexes of Group VIB metals with electrophiles and determine the feasibility of the $\eta^5 \rightarrow \eta^6$ rearrangements:[33,160]



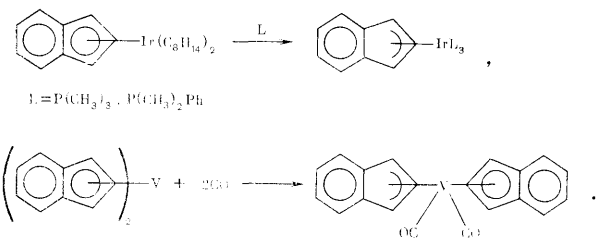
As a rule, the η^6-structures are thermodynamically preferable for chromium derivatives. The stability of the η^5-compounds increases in the sequence Cr < Mo < W.[33] The authors studied in detail the stereochemistry of the interaction of the anion η^6-$C_9H_7Cr(CO)_3^-$ (X) and the tautomeric mixture of compounds (VII) and (VIII) with alkyl halides. Investigations demonstrated the rigorous stereospecificity of these reactions: the "ricochet process" with the initial attack on the metal leads only to the *endo*-isomer, while direct attack on the carbon atom of the five-membered ring affords the *exo*-isomer. Thus the reaction of the complex (X) with CH_3I, which has been shown to proceed via the "ricochet mechanism" [compound (XI) has been isolated and characterised], leads to the *endo*-isomer (XII):[33,159]



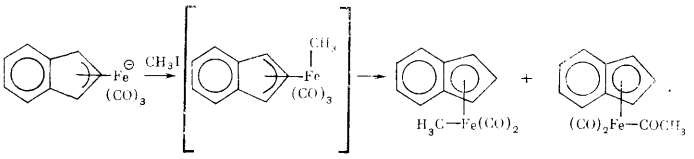
The interaction of the tautomers (VII) and (VIII) with CH_3I proceeds stereoselectively via two different mechanisms with formation of the isomers (XIII) and (XIV):[153,160,161]



The first examples of the $\eta^5 \rightarrow \eta^3$ rearrangements of indenyl complexes in the course of ligand exchange reactions were published for the first time in 1986:[109,162]



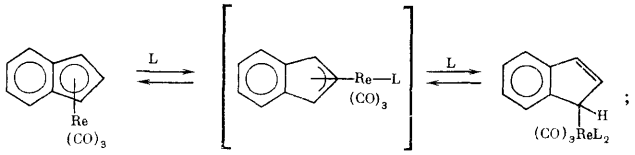
The $\eta^3 \rightarrow \eta^5$ rearrangement was described in 1987 for the reaction of an anionic iron complex with CH_3I:[163]



$\eta^5 \rightarrow \eta^1$ metallotropic rearrangements in which the type of binding of the ligand to the metal changes significantly are also known for the η^5-indenyl and η^5-fluorenyl complexes of transition metals. The ligand, previously coordinated to the metal via the π-electrons of the polycyclic system, forms a bond with the metal via the σ-electrons of one of the carbon atoms. Such rearrangements

have been described also for η^5-cyclopentadienyl compounds, but the presence of condensed benzene rings in the indenyl and fluorenyl ligands greatly facilitates these processes.

The $\eta^5 \rightarrow \eta^1$ rearrangements of carbonyl derivatives of rhenium have been reported recently.[164,165] The interaction of η^5-indenyltricarbonylrhenium with trimethylphosphine at room temperature results in the formation of a stable η^1-indenylbisphosphinerhenium complex:



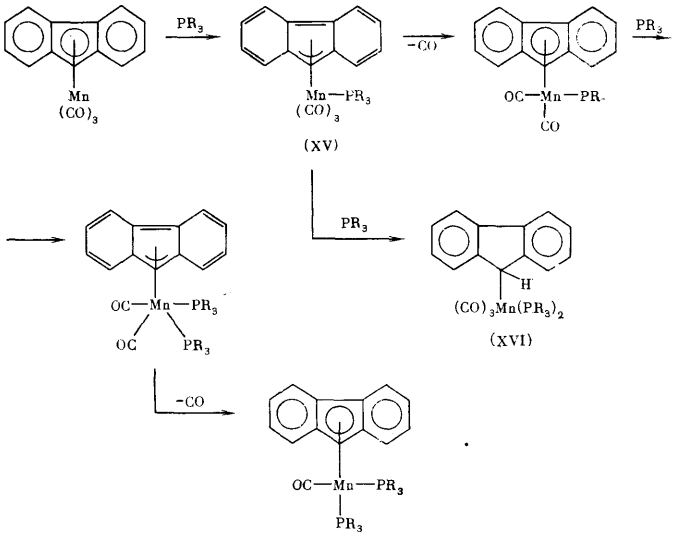
$L = P(CH_3)_3$.

A structure with η^3-linked ligand has been proposed for the intermediate compound. An analogous rearrangement has been described for η^5-cyclopentadienyltricarbonylrhenium, but the rearrangement of the η^5-indenyl complex is 10^8 times faster than for the cyclopentadienyl complex. The $\eta^5 \rightarrow \eta^1$ rearrangement of the indenyl ligand also takes place on treatment of a η^5-indenyl complex of rhodium with an excess of t-butyl isocyanate.[130]

The reverse $\eta^1 \rightarrow \eta^5$ rearrangement of the indenyl ligand has been observed in a photochemical reaction of an iron complex:[166]

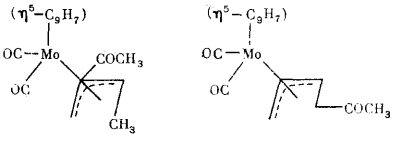
$$(\eta^5\text{-}C_9H_7)\,Fe\,(CO)_2\,(\eta^1\text{-}C_9H_7) \xrightarrow{h\nu} Fe\,(\eta^5\text{-}C_9H_7)_2 + 2CO.$$

The first instance of the $\eta^5 \rightarrow \eta^1$ rearrangement of the fluorenyl ligand has been noted in the reaction of η^5-fluorenyltricarbonylmanganese with an excess of tributyl phosphine:[167]



It has been suggested that the rearrangement proceeds as for the indenyl ligand—via the intermediate complex (XV) with the η^3-type of coordination. The structure of compound (XVI) with the η^1-fluorenyl ligand has been proposed on the basis of the ^{13}C NMR spectrum.

(c) *Ligand exchange reactions in η^5-indenyl and η^5-fluorenyl complexes of transition metals.* Extensive data have now accumulated in the literature concerning the influence of the η^5-indenyl ligand on the rate of exchange of carbonyl, olefinic, and acetylenic groups in the π-complexes of transition metals in thermal reactions. As early as 1965, it was noted that the decarbonylation of the η^5-indenyl complexes of molybdenum $RMo(CO)_3(\eta^5\text{-}C_9H_7)$ proceeds much more readily than that of the corresponding cyclopentadienyl complexes.[34] Subsequently, other studies were published in which the accelerating effect of the η^5-indenyl ligand had been observed. For example, it was noted that $[(\eta^5\text{-}C_9H_7)Mo(CO)_2(CH_3)_2C_2]^+BF_4^-$ reacts faster with PPh_3 [53] and $\eta^5\text{-}C_9H_7Mo(CO)_3CH_3$ reacts faster with but-2-yne[54] faster than their cyclopentadienyl analogues. It has also been established that methylenecyclopropane and buta-1,3-diene are inserted more readily in the $Mo-CH_3$ bond in $\eta^5\text{-}C_9H_7Mo(CO)_3CH_3$, which leads to the formation of the π-allyl complexes (XVII) and (XVIII) respectively with the simultaneous migration of a terminal CO group:[54]

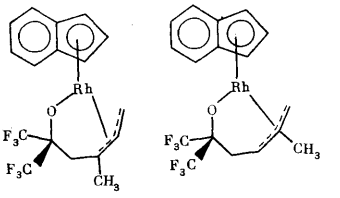


(XVII) (XVIII)

The accelerating effect of the η^5-indenyl ligand compared with the cyclopentadienyl ligand is manifested in the π-complexes of not only Group VI but also of Group VII and VIII transition metals. Especially many examples are known for rhodium derivatives. For instance, $\eta^5\text{-}C_5H_5Rh(C_2H_4)_2$ does not react with carbon monoxide, while the η^5-indenyl analogue reacts rapidly with CO at room temperature, affording $\eta^5\text{-}C_9H_7Rh(CO)_2$ in a quantitative yield.[130] The high reactivity of $\eta^5\text{-}C_9H_7Rh(C_2H_4)_2$ is also manifested in the considerable ease of the exchange of ethylene for phosphines, cycloocta-1,5-diene, 2,3-dimethylbuta-1,3-diene,[19] methylcyclopropane, acrylonitrile, t-butyl isocyanate, isoprene, cyclohexadiene, and cyclohepta-1,3,5-triene.[20,130] Similar reactions are unknown for the analogous complex with the η^5-cyclopentadienyl ligand. The substitution of the Group L in the rhodium complexes $\eta^5\text{-}C_9H_7RhL_2$ (L = CO or PPh_3) for other ligands takes place very readily (20 °C, benzene).[19] The corresponding η^5-cyclopentadienyl compounds are difficult to obtain.

Whereas only prolonged photolysis of $\eta^5\text{-}C_5H_5Rh(CO)_2$ leads to two isomeric clusters $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_3$ and in a low yield, η^5-indenyl dicarbonylrhodium is converted selectively and with a high yield into the trimer (IV) on refluxing in heptane.[59,130]

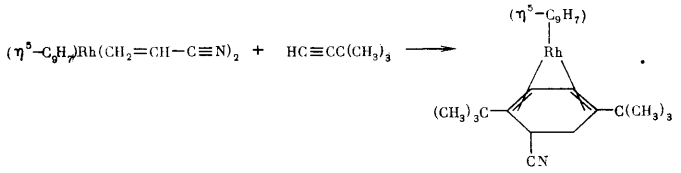
η^5-Indenyl complexes of rhodium with diene ligands exhibit an enhanced reactivity. Thus, in contrast to its η^5-cyclopentadienyl analogue, $\eta^5\text{-}C_9H_7Rh$(isoprene) reacts with $(CF_3)_2CO$ at room temperature with formation of the two isomeric products (XIX) and (XX):[168]



(XIX) (XX)

The reactions of the η^5-indenyl complexes of rhodium $\eta^5\text{-}C_9H_7RhL_2$ (L = isoprene, acrylonitrile, or 2,3-dimethylbuta-1,3-diene) with alkynes, which result in the cyclisation of acetylenes with the olefins

in the coordination sphere of the metal, are remarkable:[20,130]

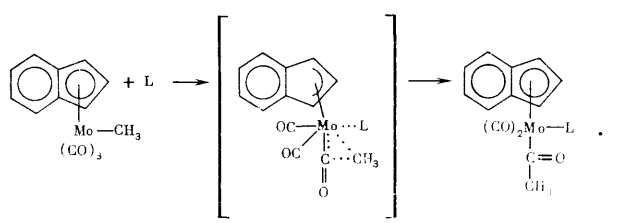


The initial stage in this reaction is the coordination of the acetylene molecule to the metal, which is facilitated by the slip of the rhodium atom along the plane of the indenyl ligand.[20]

The ready carbonylation of the $Fe-CH_3$ bond in the complexes η^5-$C_9H_7Fe(CH_3)(CO)L$ (L = CO or PPh_3) has also been described.[169]

There are many fewer examples of the accelerating effect of the η^5-fluorenyl ligand compared with the η^5-indenyl ligand. For example, it has been noted that η^5-$C_{13}H_9Co[P(OR)_3]_2$ absorbs carbon monoxide more readily than η^5-$C_9H_7Co[P(OR)_3]_2$.[17]

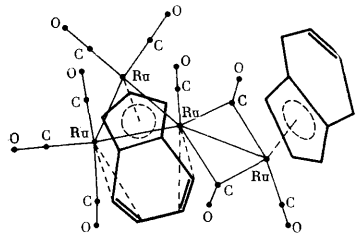
All the examples described above concern the observation of the accelerating influence of the η^5-indenyl or η^5-fluorenyl ligands on the rates of ligand exchange reactions. The first studies designed to estimate quantitatively the comparative reactivities of the η^5-indenyl and η^5-cyclopentadienyl complexes of transition metals in thermal reactions were performed in the 1970's.[170,171] The authors first explained the accelerating influence of the η^5-indenyl ligand. They carried out a kinetic study on the thermal reactions involving the substitution of CO groups by phosphines and phosphites in the molybdenum complexes η^5-$C_9H_7Mo(CO)_3X$ and η^5-$C_5H_5Mo(CO)_3X$ (X = CH_3, Cl, Br, or I) and showed that the ligand exchange proceeds via two competing mechanisms: associative and dissociative. An appreciable accelerating influence of the η^5-indenyl ligand compared with the cyclopentadienyl ligand (at least by a factor of tens and at most by a factor of hundreds of thousands) was observed in both cases. In the associative mechanism, the accelerating effect of the indenyl ligand is caused, according to the authors, by the transition to a π-allyl system, which frees an orbital of the molybdenum atom for the interaction with the nucleophile and ensures thereby the easy occurrence of the reaction via the S_N2 mechanism:



The capacity of the cyclopentadienyl ligand for π-allyl type coordination to the metal is smaller, since in the change from the η^5-coordination to the η^3-coordination in the indenyl complex the six-membered ring retains its total resonance energy, while in the case of the cyclopentadienyl ligand an isolated double bond is formed.[170] The dissociative mechanism has been studied in detail for halogenoderivatives of η^5-indenyl and η^5-cyclopentadienyl complexes.[171] In this case, the reaction rate constants were found to undergo very pronounced changes on transition to the η^5-indenyl complexes and a dependence of the rate constants on the nature of the halogen was observed:

	$C_5H_5Mo(CO)_3Cl$	$C_5H_5Mo(CO)_3Br$	$C_5H_5Mo(CO)_3I$
$k_{rel}^{10°}$	1	23	614
	$C_9H_7Mo(CO)_3Cl$	$C_9H_7Mo(CO)_3Br$	$C_9H_7Mo(CO)_3I$
$k_{rel}^{10°}$	6600	211 000	3 580 000

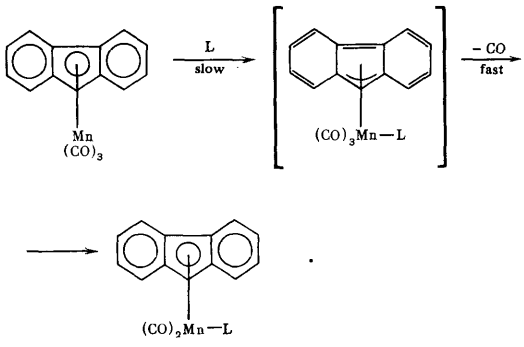
Since the absorption frequencies of the carbonyl groups in the IR spectra of the isostructural complexes η^5-$C_9H_7Mo(CO)_3X$ and η^5-$C_5H_5Mo(CO)_3X$ are almost identical, the differences between the rates of reaction are associated, according to the authors, with the appreciable change in the stability of the transition state. It has been suggested that the stabilisation of the transition state in the dissociative mechanism is achieved by the partial binding of the benzene ring of the π-ligand to the metal. In order to elucidate the role of the aromatic six-membered ring, the kinetic data for the η^5-cyclopentadienyl, η^5-indenyl, and η^5-tetrahydroindenyl complexes of molybdenum[172] and iron[173] were compared. It was found that the activation parameters and the rate constants for the tetrahydroindenyl complex η^5-$C_9H_{11}Mo(CO)_3Cl$ and η^5-$C_5H_5Mo(CO)_3Cl$ are very similar. On the other hand, the reaction rate constant for η^5-$C_9H_7Mo(CO)_3Cl$ is 6000 times greater than for the η^5-cyclopentadienyl analogue. Thus the hydrogenated six-membered ring of the tetrahydroindenyl ligand does not increase the rate of exchange of the CO groups, while the π-electron system of the condensed benzene ring participates in the stabilisation of the transition state. This is confirmed indirectly by the synthesis of the tetranuclear ruthenium cluster (XXI), since the metal atom is involved not only in η^5-type coordination to the five-membered ring but also in η^2,η^2-diene type coordination to the six-membered ring of the indenyl ligand:[174]



(XXI)

In the course of the further development of the kinetic studies on the thermal CO ligand substitution reactions in η^5-indenyl complexes of transition metals, it was shown that the rates of reaction of the indenyl complexes of rhodium η^5-$C_9H_7Rh(CO)_2$ and η^5-$(CH_3)_7C_9Rh(CO)_2$ with PPh_3 are respectively 3.8×10^8 and 6.1×10^5 times greater than for η^5-$C_5H_5Rh(CO)_2$.[175,176] The tendency of the rhodium atom to form π-allyl complexes facilitates the $\eta^5 \rightarrow \eta^3$ transitions in the associative reaction mechanism and leads to a very pronounced increase in rate, which is not observed for other metals. The quantitative effect of the η^5-fluorenyl ligand relative to the η^5-indenyl ligand in the thermal reactions of manganese carbonyl complexes with phosphines and phosphites was estimated in this connection.[167,176] It was shown that the rate of reaction with $P(OC_2H_5)_3$ in decalin is 388 times greater for η^5-$C_{13}H_9Mn(CO)_3$ than for η^5-$C_9H_7Mn(CO)_3$. The increase in the rate of substitution for the η^5-fluorenyl complex compared with the η^5-indenyl and η^5-cyclopentadienyl complexes has been explained[167] by the stabilisation of the η^3-intermediate as a result of the delocalisation of the π-electrons over all three rings, i.e. a high delocalisation energy

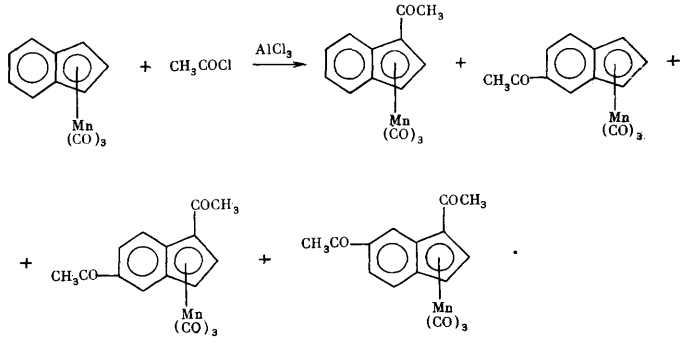
obtains in this instance.



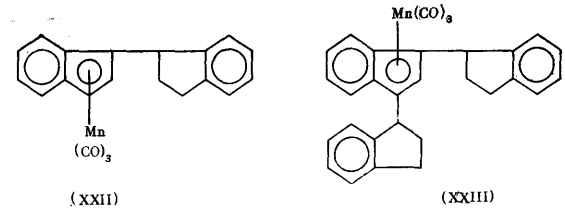
However, the accelerating effects of the η^5-indenyl and η^5-fluorenyl ligands is not always maintained. Thus the effect has not been observed in the photochemical substitution of the carbonyl groups in manganese complexes for triphenylphosphine.[177] The rate constants for the complexes $LMn(CO)_3$, where L = η^5-C_5H_5, η^5-C_9H_7, and η^5-$C_{13}H_9$ are 6.0×10^{-3}, 5.2×10^{-3}, and 3.8×10^{-3} min^{-1} respectively.

(d) *The hydrogen substitution reactions in η^5-indenyltricarbonyl and η^5-fluorenyltricarbonyl complexes of manganese and rhenium.* The hydrogen substitution reactions in the π-ligands of neutral η^5-indenyl and η^5-fluorenyl complexes of transition metals have been little investigated. Attempts to benzoylate η^5-cyclopentadienyl (η^5-indenyl)-iron with benzoyl chloride in the presence of $AlCl_3$ and also to metallate it by n-butyl-lithium were reported in 1964.[47] However, acylation led to the decomposition of the complex and treatment with n-C_4H_9Li and subsequently with D_2O led to the isolation of the non-deuteriated initial compound.

A series of studies[178–180] on the electrophilic and protophilic substitution η^5-indenyl and η^5-fluorenyl ligands of manganese and rhenium complexes were published in 1982–1985. It was shown that, in the interaction of η^5-$C_9H_7Mn(CO)_3$ with an excess of CH_3. .COCl in the presence of $AlCl_3$ in methylene chloride, hydrogen is substituted by $COCH_3$ in both the five-membered and six-membered rings of the η^5-indenyl ligand:[178]



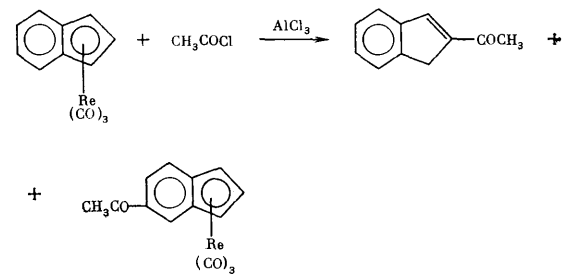
Similarly, in the isotope exchange of hydrogen involving η^5-C_9H_7. .$Mn(CO)_3$ on treatment with a mixture of the acids CF_3COOD and D_2SO_4 in CH_2Cl_2, hydrogen is replaced by deuterium in both rings of the π-ligand, although the substitution in the five-membered ring predominates. Apart from the deuteriated derivative, the deuterium-containing complexes (XXII) and (XXIII) were isolated in this reaction. These complexes are apparently formed as a result of the alkylation of the initial compound by the indene protonated in the acid medium, produced as a result of the cleavage of the metal–π-ligand bond.



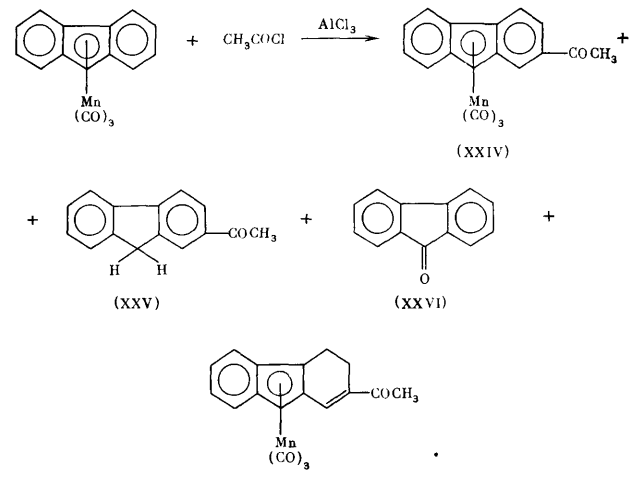
(XXII) (XXIII)

In order to compare the reactivities of the η^5-indenyl and η^5-cyclopentadienyl ligands, the competitive acetylation of η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_5H_5Mn(CO)_3$ was carried out.[180] It was established as a result that the reactivity of the η^5-indenyl ligand is on the whole much higher than that of the η^5-cyclopentadienyl ligand. However, when the reactivity of only the five-membered ring of the η^5-indenyl ligand is compared with that of the η^5-cyclopentadienyl ligand, then the differences are insignificant.

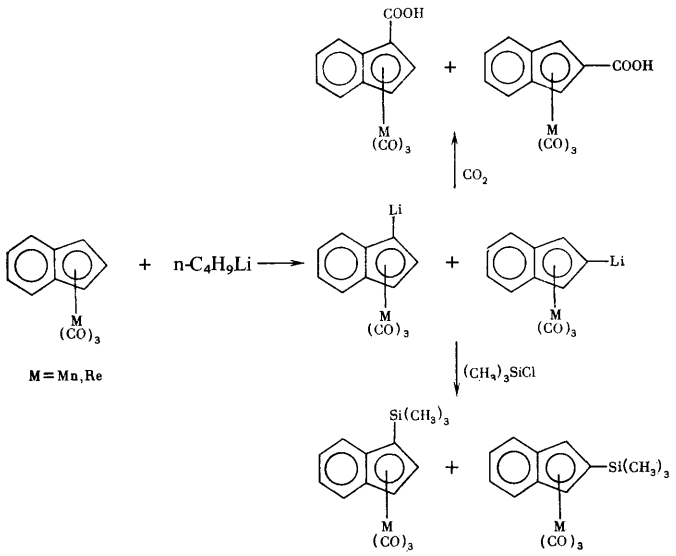
In contrast to η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_5H_5Re(CO)_3$, the acetylation of η^5-$C_9H_7Re(CO)_3$ [4] takes place mainly with abstraction of the π-ligand. Thus, after treatment with acetyl chloride in the presence of $AlCl_3$ in CH_2Cl_2, the complex (5-$CH_3COC_9H_6$)$Re(CO)_3$ (5%) and 2-acetylindene (17%) were isolated:[178]



The acetylation of η^5-$C_{13}H_9Mn(CO)_3$ takes place only in the six-membered ring of the π-ligand and is also accompanied by the dissociation of the metal–π-ligand bond. The acylated complex (XXIV) (40%), the products (XXV) and (XXVI) resulting from the elimination of the π-ligand, and the partly hydrogenated complex (XXVII) (6%) are formed:



Metallation of η^5-indenyl complexes of manganese and rhenium with n-butyl-lithium in THF involves only the five-membered ring of the indenyl ligand with formation of a mixture of the 1- and 2-isomers:[179]

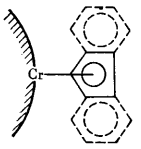


For the quantitative estimation of the comparative reactivities of the η^5-indenyl and η^5-cyclopentadienyl complexes, Lobanova et al.[180] carried out the competitive metallation with n-butyl lithium of mixtures of the following pairs of compounds: η^5-$C_9H_7MnCO_3$ and η^5-$C_5H_5Mn(CO)_3$; η^5-$C_9H_7Re(CO)_3$ and η^5-$C_5H_5Re(CO)_3$; η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_9H_7Re(CO)_3$; η^5-$C_5H_5Mn(CO)_3$ and η^5-$C_5H_5Re(CO)_3$. It was established that the η^5-indenyl complexes are somewhat more reactive than the corresponding η^5-cyclopentadienyl complexes, although the differences are slight. It was also discovered that the rhenium complexes are metallated much more readily than the manganese complexes, which has been explained by the greater tendency of the rhenium compounds to undergo protophilic substitution reactions.[180]

(e) *Catalytic properties of η^5-indenyl and η^5-fluorenyl complexes of transition metals.* The "coordination flexibility" of the η^5-indenyl and η^5-fluorenyl ligands, which accelerates the ligand exchange reactions in transition metal complexes, may be important when they are used as homogeneous catalysts of chemical processes where the lability of the ligands at the metal atom is significant.

The catalytic activity of η^5-indenyl complexes of transition metals has been reported in a number of studies. For example, the interaction of η^5-$C_9H_7Rh(C_2H_4)_2$ with an excess of acetylenes leads to the catalytic cyclotrimerisation of 3,3-dimethylbut-1-yne to 1,2,4-tri-t-butylbenzene, while but-2-yne is cyclotrimerised to hexamethylbenzene.[130] Furthermore, η^5-$C_9H_7Rh(C_2H_4)_2$ is a catalyst of the isomerisation of allyltrimethylsilanes to *trans*-propenyltrimethylsilanes.[181] Dinuclear rhodium complexes with indenyl ligands are also effective catalysts in the trimerisation of acetylenes.[182] The high catalytic activity of η^5-indenyl derivatives of Group IVB metals $(\eta^5\text{-}C_9H_7)_2M$ (M = Ti, Zr, or Hf) in the polymerisation of α-olefins has been noted.[183]

Studies have been made on the catalytic properties of di-indenyl- and difluorenyl-chromium complexes deposited on silica gel.[184] Like chromocene, these complexes exhibited a catalytic activity in the polymerisation of ethylene. It is believed that the polymerisation proceeds via an anionic mechanism and that the catalyst active centre is the chromium centre (XXVIII):



The increased thermal stability of the indenyl catalyst compared with the cyclopentadienyl catalyst has been noted. It has been indicated in patents[185,186] that η^5-$C_9H_7Mn(CO)_3$, η^5-$C_{13}H_9Mn(CO)_3$, as well as η^5-$C_5H_5Mn(CO)_3$ can be used as anti-knocking agents. It has been shown that the η^5-indenyl and η^5-fluorenyl derivatives of titanium L_2TiCl_2 (L = η^5-C_9H_7 or η^5-$C_{13}H_9$) as well as their η^5-cyclopentadienyl analogues exhibit an anticancer activity.[187]

III. CONCLUSION

Thus the data examined above show that η^5-indenyl and η^5-fluorenyl complexes of transition metals have a number of characteristic features apart from their great similarity to their cyclopentadienyl analogues. Thus the strength of the π-ligand–metal bond varies in the sequence η^5-cyclopentadienyl > η^5-indenyl > η^5-fluorenyl, which leads to a decrease in the stability of the indenyl and fluorenyl compounds. Furthermore, some distortion of the η^5-type coordination is observed for the η^5-indenyl and η^5-fluorenyl complexes, which is reflected in the difference between the lengths of the bonds linking the metal to the carbon atoms of the five-membered ring. On treatment of the η^5-indenyl and η^5-fluorenyl derivatives with certain reagents, a change in the type of coordination to the transition metal from η^5- to η^6-coordination and from η^3- to η^1-coordination has been observed, i.e. intramolecular metallotropic rearrangements are characteristic of such compounds. The fact that the rates of thermal ligand exchange reactions of the η^5-indenyl and η^5-fluorenyl complexes exceed by several orders of magnitude the rates of reaction of the η^5-cyclopentadienyl compounds may be of special interest from the practical point of view.

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Microlayer and Glass Formation in Block Copolymers

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The present state of the theoretical and experimental studies on one of the possible types of phase transformations in block copolymers, namely microlayer formation, as well as the influence on the latter of vitrification is surveyed. It is shown that microlayer formation leads to the appearance of supermolecular structures whose parameters depend on the composition, temperature, and the number and length of the blocks; microlayer formation also determines the vitrification parameters, which can in their turn inhibit the microlayer formation. The mutual influence of microlayer and glass formation processes is discussed.
The bibliography includes 165 references.

CONTENTS

I. Introduction 981
II. Separation into microphases in the melt 981
III. Mutual influence of microlayer and glass formation 991

I. INTRODUCTION

Block copolymers (BP) is the name usually given to substances whose linear macromolecules consist of fragments of homopolymers (blocks) linked covalently via their ends (Fig.1). Depending on the primary chain structure, the chemical structure of the monomer units, the length of the blocks, their number and distribution in the chain, and their flexibility, various phase transformations can take place in BP: separation into microphases in the melt, crystallisation (fusion), polymorphic transitions, liquid crystal ordering. Furthermore, the non-crystalline component is capable of vitrifying. The phase transformations in BP take place in many respects analogously to the phase transitions in mixtures, but the presence of a covalent bond between the components leads to a number of characteristic features, which differentiate BP as a separate class of multi-component systems.

This review is devoted to the consideration of one type of transformations in BP—microlayer formation—and its dependence on the primary structure of the macromolecule. The mutual influence of microlayer and glass formation processes is also discussed.

The study of phase transformations in BP is not only of purely theoretical interest but is also essential in connection with their possible application in the development of experimental techniques (neutron radiation monochromators, materials for microelectronics, and conductors several tens of angstroms in diameter), in medicine, and in industry (gas- and liquid-separating membranes, constructional materials). Since BP constitute the simplest models of a heteropolymer, the study of the phase transformations in them is also useful for the understanding of the processes occurring in biological structures (in particular, in cell membranes).

A BP constitutes a special case of a heteropolymer, i.e. a polymer made up of monomers having different chemical structures, and the description of the primary structure of an isolated heteropolymer macromolecule is analogous to the description of the structure of biopolymers.[1-7] We shall not dwell on the fundamental theoretical questions concerning the amount, complexity, and value of the information inherent in heteropolymers,[2,3,7] while questions relating to the selection and calculation of self-averaging quantities have already been discussed.[8,9] In the present review, we shall merely consider briefly the quantitative differences between the degrees of order in the intramolecular components,[10] such order influencing the parameters of the phase transformations. (The distribution of the intermolecular components characterises the feasibility of phase transformations at the intermolecular level and the difference between the structures of the macromolecules characterises their feasibility at the macroscopic level.)

The existing classification includes four types of linear synthetic heteropolymers: (1) periodic block copolymers; (2) statistical copolymers (SP), whose macromolecule is usually represented as one in which there is a non-ordered distribution of the monomers; (3) gradient (or conical) BP in which there is a SP block between two homopolymer blocks; (4) statistical BP in which the blocks are joined up statistically (a SP is a special case of such BP); the differences between the primary structures are specified by the methods and conditions of synthesis.

In the present review, the term block copolymer is understood (in contrast to the exact definition given previously) as a polymer whose linear chains are made up of blocks consisting of a continuous sequence of monomers of one kind, the average length of the blocks (with respect to the assembly of primary chain structures) being significantly greater than the standard deviation characterising the scatter of the blocks with respect to their lengths. We shall consider below only BP (type 1) and their blends, while blends of BP with homopolymers, statistical and gradient SP, as well as low-molecular-weight solvents are not included in the review.

II. SEPARATION INTO MICROPHASES IN THE MELT

A number of reviews have been devoted to the separation into different phases in BP melts.[11-19] However, in recent years much new information has been published, which permits a deeper understanding of the nature of this phenomenon. We shall therefore describe only briefly the information which has already become generally known and the main analysis will be devoted to studies carried out in recent years.

Like blends, BP are capable of separating into different phases. The fundamental difference between the phase separation in BP and the separation in blends consists in the fact that the characteristic size of the species and of the phase is of the order of several radii of inertia of the block and, depending on the length of the block, can

vary from several nanometers to several tens of nanometers. Separation into layers in BP occurs for dimensions of the phase species less than the length of the macromolecule and is an intramolecular process (Fig.1), so that it is referred to as microphase layer formation. Here one of the phases represents a monoconnected region (matrix) whilst the other constitutes a polyconnected region, i.e. one consisting of a large number of bounded domains, alternatively both phases can be polyconnected (alternating lamellae), or both phases can be monoconnected (interpenetrating phase networks).

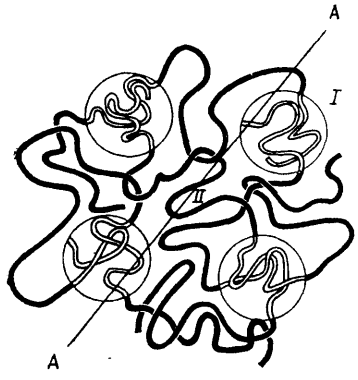


Figure 1. Schematic representation of the supermolecular structure of a periodic BP separated into pure microphases:[16] (I) phase consisting of spherical domains incorporating type 1 blocks; (II) phase constituting a monoconnected matrix consisting of type 2 blocks; $A-A$—straight line along which the concentration profile is determined.

Prolonged annealing leads to the improvement of the domain structure of the BP but does not entail the coalescence of the domains, as happens in blends. The improvement of the BP structure during annealing consists in the fact that in periodic BP the supermolecular structure (SMS), made up of domains having different relative positions, may become strictly regular, resembling the disposition of atoms at the crystal lattice sites of a crystal of a low-molecular-weight compound,[20,21] as a result of which such SMS is sometimes referred to as a supercrystal.[22] Thus one may say that microlayer formation in BP is analogous to separation into layers and supermolecular crystallisation.†

The phase state of BP is characterised by the spatial distribution of the concentrations of its components. The straight line passing through the BP ($A-A$ in Fig.1) determines the curve representing the distribution of concentration which is referred to as the concentration profile (Fig.2). The form of the profile, which can be characterised by its parameters, namely the amplitudes (phase compositions) Φ' and Φ'', the thicknesses of the domains T' and T'' and of the interfacial layer Δ, and the period D, depends in the general case on the temperature and the molecular weight distribution (MWD) of the blocks and also on the position of the straight line specified in space. We shall consider separately the influence of temperature and MWD on the parameters of the concentration profile and also on the symmetry of the SMS.

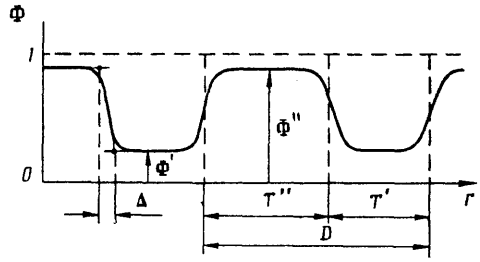


Figure 2. Second component concentration $\Phi = \Phi_2$ profile along a certain specified direction (r = distance); Φ' and Φ''—contents of the second component (concentration amplitudes) in phases I and II respectively; T' and T''—microphase thicknesses; D—SMS period; Δ—thickness of the interface.

1. Transition from the Non-ordered State to the State Separated into Microlayers

At sufficiently high temperatures or for sufficiently small lengths of the blocks r_1, the BP can exist in a single-phase (non-ordered) state. A decrease in temperature or an increase in r_1 should lead to a transition across the microphase separation boundary (MSB), provided, of course, that another phase transition or vitrification does not occur before that. In the general case, the MSB is represented by a curve in terms of the variables T, Φ_i, r_i or χ, Φ_i, r_i (χ is the Huggins interaction parameter, T the temperature, Φ_i the volume fraction of the ith component, and r_i the degree of polymerisation of the ith component block, and $i = 1-n_{ia}$, the number of intramolecular components).

Some of the qualitative features of the MSB are manifested when the method of geometrical thermodynamics is applied to the BP.[10,23-26] By analogy with blends, one can assume that, for a fixed composition of the BP, the compositions of the coexisting phases vary with temperature in conformity with the binodal curve in the temperature–composition plane. Since in binary periodic BP the intermolecular composition (the content of the second component) is defined by the formula

$$x \equiv x_2 = M_2/[a(n)M_1 + M_2] \qquad (1)$$

[M_1 and M_2 are the molecular weights of blocks 1 and 2 and $a(n)$ is a coefficient which depends on the number of blocks and, for branched BP, on the way in which unlike blocks are joined together], the construction of the temperature–composition diagram requires the variation of the molecular weight (MW), i.e. r_i, of the blocks, for example, by varying M_2 for a constant M_1. As for blends, a displacement and deformation of the binodal curve should then occur.

For a geometrical representation of the dependence of the position and form of the binodal curve on the MW, it is necessary to introduce a third coordinate (M_2) in addition to T and x, and M_1 should be regarded as a parameter (Fig.3). In the $T-x-M_2$ three-dimensional state, the binodal curve unfolds into the binodal surface

† BP separated into microphases are sometimes classified as lyophilic liquid crystals.[18]

and the composition defined by Eqn.(1) is represented geometrically by a curve in the $x-M_2$ plane. The MSB is then represented by a spatial curve defined by the intersection of the binodal surface with a curvilinear cylinder with the composition curve at its base. It is sometimes convenient to adopt as the MSB the projection of this curve onto the $T-x$ or $T-M_2$ plane. Such geometrical representation reveals that, firstly, the microlayer formation critical point for monodisperse BP is not displaced to the left of the maximum although it is located on the MSB; secondly, for certain relations governing the form of the binodal surface, which is determined by the nature of the components and the curvature of the composition curve, a second maximum can appear on the MSB, being located to the right of the maximum; thirdly, one cannot rule out the possibility of the existence of a single-phase state when M_2 increases very markedly.[23-26]

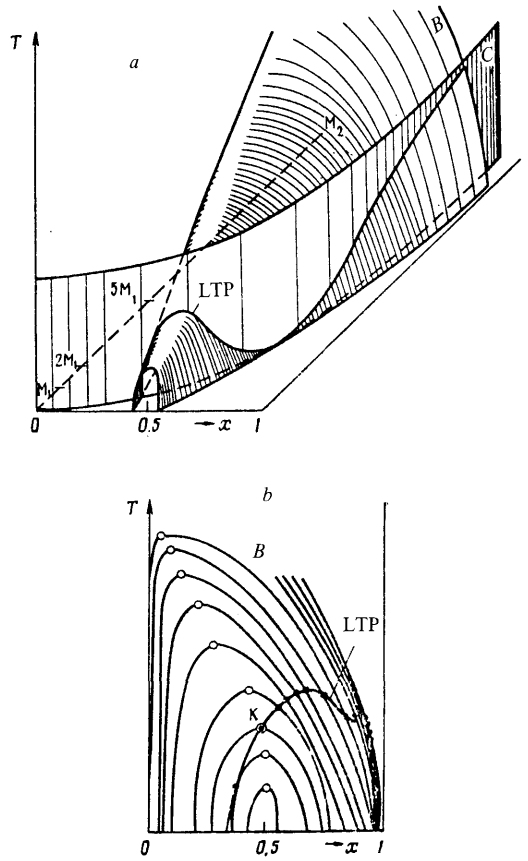


Figure 3. Construction of the locus of the turbidity points (LTP) for BP with M_1 = const. by the surface intersection method:[26] (a) three-dimensional representation in terms of the coordinates $T-x-M_2$ [B—binodal surface; C—curved cylinder, with generator parallel to the temperature axis, whose base is the overall composition curve $x = x(M_2)$]; (b) two-dimensional representation in the $T-x$ plane {B—family of binodal curves corresponding to different values of M_2 [with increase in M_2, the consolute point K (open circles) is displaced upwards]; LTP—projection of the three-dimensional LTP onto the $T-x$ plane}.

Microphase separation is possibly only in those heteropolymers in which the intermolecular components have been "mixed" along the chain to a sufficiently slight extent, i.e. the primary chain structure is closer to BP than to SP.[34] The conditions imposed on the primary BP structure to achieve microlayer formation have the form

$$\overline{R^2N^2}/\overline{N^2} > \overline{R_1^2N_1^2}/\overline{NN_1} + \overline{R_2^2N_2^2}/\overline{NN_2},$$
$$\overline{k_{12}}/\overline{N} < 2\,(\overline{N_1}/N)\,(\overline{N_2}/\overline{N}),$$

where $N_i(S)$ is the number of units of the ith kind in a macromolecule of type S, $N(S) = N_1(S) + N_2(S)$, $R_i^2(S)$ and $R^2(S)$ are the squares of the radii of inertia of the units of the ith kind of the macromolecule of S and of all the units respectively averaged with respect to the conformations, and $\overline{k}_{12}$ is the average number of bonds between unlike units (heterobonds) per macromolecule. The bars above the symbols denote averaging with respect to the molecular-structural distribution in the system: $\overline{A} = \sum_s n_s A(S)/\sum_s n_s$, where

n_s is the number of macromolecules of type S, which can be specified by their structural formula, per unit volume.

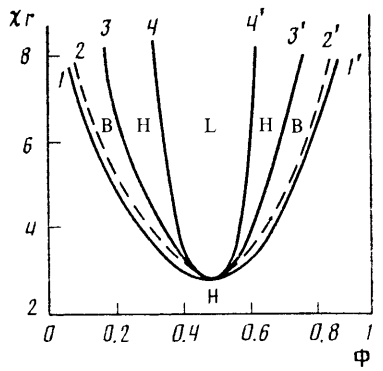


Figure 4. Phase diagram for a di-BP:[33,37] (1,1′) microphase separation boundary; (2) and (2′) spinodal curve; (3) and (3′) boundary corresponding to the transition from the body-centred cubic SMS (B) to the hexagonal SMS (H); (4) and (4′) boundary of the transition from the hexagonal SMS to the lamellar SMS (L); N—non-ordered phase.

For di-BP, the MSB has been calculated analytically both near the critical point[33] and at a distance from it.[37] These data supplement one another and make it possible to construct the complete phase diagram of the di-BP[37] (Fig.4). In a study,[33] based on Landau's theory of phase transitions, the free energy was defined by a series expansion in terms of powers of the order parameter $\psi(r)$:

$$\psi(\mathbf{r}) = \langle \delta\Phi_1(\mathbf{r}) \rangle \equiv \langle \Phi_1(\mathbf{r}) - \Phi_1 \rangle,$$

where $\Phi_1(\mathbf{r})$ is the ratio of the local density of type 1 monomers at the point $\mathbf{r}$ to the overall density of the monomers averaged with respect to the specimen (for a non-compressible system, Φ_1 corresponds to the concentration); the angular brackets denote averaging with respect to the Gibbs *ensemble*. The MSB was represented in the above study[33] by the dependence of χ' on composition. For $\Phi \neq 0.5$, the phase transition is a first-order transition, since the

order parameter varies abruptly.[33,37] For $\Phi = 0.5$, Landau's theory predicts a second-order transition, but at this point the concentration fluctuations with $|\mathbf{k}| \neq |\mathbf{k}^*|$, which can restore the first-order transition, should begin to play a role.[33] The above features of the thermodynamic behaviour of BP are associated with the fact that the spectrum of concentration fluctuations has a maximum at $k = k^*$, which is infinitely high on the spinodal curve. Several workers have noted simultaneously that fluctuations with $k^* \neq 0$ should grow in the vicinity of the spinodal curve.[33–36]

The range of temperatures and compositions where the BP is in the homogeneous state while blends of homopolymers with the same MW of the components have already separated into layers has been predicted theoretically.[33,38] This conclusion agrees with the results of experiments carried out on blends and polyblock BP.[39]

An important theoretical prediction is that the binodal and spinodal curves are close to one another,[33] which makes it possible to consider the influence of the primary structures of the macromolecules on the MSB as being the same as the influence on the spinodal curve, which is easier to calculate. The influence of the number of blocks and the way in which they are joined together and also of the polydispersity of the MW on the position of the spinodal curve has been examined.[34,40] The closeness of the spinodal curves for BP and homopolymers has been predicted and on the $T-x$ plane the spinodal curve for the BP lies below the spinodal curve for the blend, which agrees with conclusions reached in other studies.[33,38,39] An increase in the degree of asymmetry $s = r_1/(r_1 + r_2)$ of the tri-BP $A_{r_1}B_{r_2}A_{r_1}$ macromolecule and the increase in the number of blocks in periodic polyblock BP reduce the spinodal temperature T_{sp}.[34] A decrease in the fraction of long chains in a binary blend of monodisperse di-BP, differing in chain length, or in the polydispersity coefficient $P = r_w/r_n$ for a polydisperse BP also results in a smooth decrease in T_{sp} (increase in χ_{sp}).[40]

Hitherto, we have discussed the position and shape of the MSB itself, but BP have characteristic features also when the MSB is approached from the side of the single-phase region. It has been shown theoretically[41] and experimentally[42] that the "correlation hole" effect is observed in this region and leads to the appearance of a scattering maximum on the angular dependences of the intensities of X-rays and thermal neutrons. The value of k corresponding to the correlation hole has been predicted by the statistics of ideal chains. This effect is sensitive to the degree of polydispersity of the BP. The values of χ have been determined from the position of the scattering maximum by the method proposed by Leibler[33] and proved to depend on the composition in the region where they are low.

The prediction of the formation, as the MSB is approached from the side of the single-phase state, of a rarefied micelle gas, which becomes ordered only when its density increases, made[43] on the hypothesis of the mutual repulsion of the micelles, has been disproved[37] by demonstrating the existence of a region where the micelles attract one another. The formation of ordered structures made up of micelles should occur abruptly (first-order transition) without the formation of unified micelles. In order to reach a final conclusion, it is necessary to test experimentally the claims concerning the sign of the interaction of the micelles.

All the theoretical studies discussed in this review were performed on the assumption that there are no directed intermolecular interactions. However, the position and shape of the binodal surface for BP as well as for mixtures of low-molecular-weight liquids[27–30] must depend on the energy, direction, and degree of degeneracy of various intermolecular bonds, which may be formed both between the molecules of one component and between the molecules of different components. By analogy with mixtures, one can postulate that, when different types of intermolecular interactions are considered, the phase diagram for the BP may have a different lower consolute temperature and can contain loops, "compressed" loops, "compressed" domes, etc. On the other hand, covalent bonding can lead to additional changes in the phase diagram. The influence of directed intermolecular bonds on the shape of the MSB requires both theoretical and experimental study.

As a consequence of the complexity of the experimental investigation of the composition of the coexisting phases in microheterogeneous systems, no binodal curve for a real BP has been obtained hitherto. The optical methods and sample methods, employed to construct the binodal curves for these systems, are relatively ineffective or inapplicable. The low-angle X-ray and neutron scattering methods have been used so far only for the qualitative estimation of the segregation coefficient[31] but not for the quantitative measurement of the compositions of the coexisting phases. Apart from the diffraction methods, calibration relations between the glass point and the composition of the single-phase system[10,23–25] and also experimental $\chi(x,T)$ relations can be used to determine the phase composition.

2. The Symmetry and Repeat Period of the Supermolecular Structure

(a) The Influence of Temperature

It is known from early experimental data that the symmetry of the SMS varies as the intermolecular composition of the BP is varied.[18] The change in symmetry also as the temperature is altered has been predicted theoretically recently.[33,37] Semenov's theory[37] is valid in the region where $\chi_r \gg 1$, while Leibler's theory,[33] based on Landau's theory, is valid in the region where $(\chi_r)_{cr} = 2.62$. Thus the two theories supplement one another. With increase in χr (i.e. with decrease in temperature or with increase in the degree of polymerisation), a body-centred cubic SMS made up of spherical domains‡ should be formed immediately beyond the MSB and, under conditions such that $(\chi r)_1 > (\chi r)_{sp}$ [where $(\chi r)_{sp}$ represents the values of χr along the spinodal curve and $(\chi r)_1$ represents the values on the boundary corresponding to the transition from the body-centred to the hexagonal structure], is transformed into a hexagonal SMS made up of cylindrical domains; the latter is in its turn converted into a lamellar SMS for $\chi r = (\chi r)_2$ and then the structures are inverted, i.e. in the domains component 1 is replaced by component 2 and conversely (Fig.5). The transition from one type of SMS to another is a first-order phase transition. Although $(\chi r)_1 > (\chi r)_{sp}$, over a wide range of compositions ($0.2 < \Phi < 0.8$) these values are very close.

Since in the region of the diagram between the binodal and spinodal curves the formation of a microphase structure is very slow, the body-centred cubic SMS should be metastable. This may serve as an explanation of the absence of direct observations of the body-centred cubic SMS much below the microlayer formation temperature; we may note that the absence of such observations can be

‡ In contrast to Semenov's[33] and Leibler's[37] theories, the theory of Helfand and Wasserman[47] predicts a transition to an SMS with a face-centred cubic lattice made up of spherical domains.

accounted for also by the high stability of the face-centred cubic SMS (see the last footnote). These hypotheses require experimental confirmation. It may be expected that body-centred cubic SMS are easier to observe for low and high values of Φ (for $\Phi < 0.2$ or $\Phi > 0.8$), since in this case the difference $(\chi r)_1 - (\chi r)_{sp}$ is considerable and the temperature range corresponding to the stability of such SMS expands significantly. When the blocks are highly incompatible ($\chi r_1 \gg 1$), the transition from the spherical SMS to the cylindrical SMS occurs at $\Phi_1 = 0.12$ and that from the cylindrical to the lamellar SMS takes place whence $\Phi_2 = 0.28$.[37] The sequence of the changes in the SMS as Φ is varied from χr = const. agrees with thoroughly established empirical data.[11,13,18]

The formation of a SMS of the supercritical type depends on the preparation conditions. A structure of the paracrystalline type is frequently formed in which there is only short-range order in the arrangement of the domains and long-range order is absent;[45] such structures generate a single diffuse ring on low-angle X-ray diffraction patterns. The X-ray diffraction pattern of the supercrystal is characterised by a rigorously symmetrical distribution of localised reflections up to fairly high orders.[20,21,46] With increase in annealing time above the glass points of the components, the SMS is improved, which increases the number of reflections and their sharpness.[21]

The transitions between different types of symmetry of the supercrystal have been poorly investigated experimentally, but a series of studies have been published recently[48-58] on the disappearance of the SMS with increase in temperature. Their main results are presented in Table 1. Most of the experiments were performed on the polystyrene–polyisoprene and polystyrene–polybutadiene BP; precautions were taken to eliminate thermal degradation, which is known, from studies on blends of homopolymers,[59-61] to be capable of modifying greatly the phase diagram. The principal finding, which agrees with the theory, is the disappearance of the SMS with increase in temperature and also with decrease in the MW (even at room temperature[62]). The authors explain the disappearance of the SMS either as the breakdown of the ordered SMS or as the mixing of the components.

The disruption of the SMS was accompanied by characteristics which can be divided into two types: (1) a decrease in the number of small-angle Bragg reflections without change in the long period; (2) a decrease in the number of reflections with increase in the long period by a factor greater than 2 before the disappearance of the SMS. A decrease in the long period has been noted only for lamellar supercrystals (not in all the experiments), while for other types of SMS the periodicity vanishes without change in the period. Studies on the kinetics of the thickening of the lamellae have shown that the weight of the latter increases with increase in temperature and with decrease in MW.[55] One can therefore postulate that in certain cases the long period increases during a time shorter than the duration of the experiment. Qualitatively this hypothesis has been confirmed by the sudden disappearance of the long period from BP with a low MW (Table 1). Within the framework of the existing ideas, it is not altogether understood why the thickening in lamellar supercrystals begins at approximately the same temperature regardless of the MW. In order to elucidate the nature of the disappearance of the ordered SMS, further experimental studies are essential.

Certain hypotheses, which have not been discussed hitherto, can be put forward concerning the influence of temperature on the concentration profile and symmetry of SMS. With increase in temperature, the difference $\Delta x = x'' - x'$ diminishes; this should be accompanied by a transition of the block from one phase to another.

Table 1. The influence of temperature on the parameters of the SMS of the block copolymers.

No.	Primary structure (10^{-3} MW)	x_2/P	SMS	Method	Type of temperature singularity	Refs.
1	PS-PI (51-47)	0.48/1.30	lamellae	SAXS	weak l/p maximum at 383 K and its marked growth in the range 453-523 K, after which it disappears	[53]
2	PS-PI (187-33)	0.15	PCP, PI spheres	SAXS	there are no singularities in the range 293-453 K	[52]
3	PS-PI			SAXS, EM	l/p disappears at 463 K; growth of l/p above 473 K	[55]
	(13.5-13.5)	0.5/1.25				
	(25.5-25.5)	0.5/1.20				
	(36-36)	0.5/1.15	lamellae			
	(49-49)	0.5/1.30				
4	PS-PB (7-20)	0.75/1.04	PS spheres	SAXS	l/p disappears at ~423 K	[50]
5	PS-PEO (14-20)	0.59/1.15	lamellae	SAXS, PM	l/p disappears at 433 K	[87]
	(22-10)	0.32/1.15	HEX, PEO cylinders		l/p disappears at 403 K	
	(22-53)	0.71/1.15	HEX, PS cylinders		l/p disappears at 308 K	
6	PS-PVTMS (97-89)	0.52/–	–	PE	CPE maximum at 500 K	[166]
7	PS-PI-PS (16-12-16)	0.38/–	lamellae	DMA, SAXS	sharp fall of viscosity and of modulus of elasticity at 498 K, disappearance of l/p at 513 K	[48]
8	PS-PI-PS (8-35-8)	0.68/1.25	FCCP, PS cylinders	SAXS	disappearance of reflections at 426 K	[54]
9	PS-PI-PS			SAXS	marked growth of l/p above 473 K	[55]
	(16-32-16)	0.5/1.30	lamellae			
10	PS-PB-PS (7-43-7)	0.77/–	HEX, PS cylinders	EM, DMA	disappearance of microheterogeneity between 398 and 463 K and fall of dynamic viscosity at 423 K	[49]
11	PS-PB-PS (7-43-7)	0.77/–	ditto	DSC	annealing at 563 K leads to disappearance of vitrification of PB	[51]
12	PS-PB-PS (7-43-7)	0.75/–	BCCP, PS spheres	SAXS	disappearance of l/p at 513 K	[50]
13	PS-PB-PS (10-55-10)	0.73/–	PS cylinders	PE	CPE maximum at 400 K	[50]
14	PS-PB-PS	0.55/–	–	PE	CPE maximum at 393 K	[167]

Notation: P = M_w/M_n = polydispersity coefficient, PS = polystyrene, PI = polyisoprene, PB = polybutadiene, PEO = poly(ethylene oxide), PVTMS = polyvinyltrimethylsiloxane, PCP = primitive cubic packing, FCCP = face-centred cubic packing, BCCP = body-centred cubic packing, SAXS = small-angle X-ray scattering, EM = electron microscopy, PM = polarisation microscopy, DMA = dynamic mechanical analysis, DSC = differential scanning calorimetry, PE = photoelasticity, CPE = coefficient of photoelasticity, l/p = long period observed for small X-ray and thermal neutron scattering angles, HEX = hexagonal packing.

Such transitions can occur via two pathways: (1) as a result of the rotation of the macromolecule by 180° about the junction between the blocks, so that blocks of different kinds change places simultaneously; (2) as a result of the "folding" of the macromolecule, i.e. a transition to another phase of only a block of one kind (in this instance the heterobond need not necessarily remain at the interface).§ The predominance of one mechanism over the other should

§This mechanism has also been proposed and examined in a recent communication.[63]

depend on temperature and on the primary structure of the macromolecule.

With increase in temperature, the amplitude of the elastic waves which have developed on the surfaces of the domains increases owing to the increase in the role of thermal fluctuations and the decrease in surface tension. These excitations can become collective and can lead to fluctuations in the form of the domains and to the fluctuation overlapping of neighbouring domains as a consequence of their relative proximity. The stability of the superlattice can therefore be diminished before the molecular mixing of the components take place. As a consequence of the decrease in stability, the long period disappears before the components are completely mixed. For this reason, it would be premature to combine the concepts of the fusion of the superlattice and mixing, as suggested by Leibler.[33]

The ordered SMS has a characteristic period which depends on the molecular parameters. Theory predicts the following expression for the period which is valid for three structures (spherical, cylindrical, and lamellar):

$$D = z a r^{2/3} \chi^{1/6},$$

where a is the effective radius of the inertia of one unit; $z = 3.5\Phi^{1/3}$ for the spherical domains, and $z = 4(3/\pi^2)^{1/3}$ for the lamellar SMS.[37] The $D \propto r^{2/3}$ relation for the lamellar structure has also been predicted by the scaling method.[64,65] However, the $D \propto r^{0.643}$ and $D \propto r$ relations have been predicted[66] for high and low MW respectively. We may note that the theory[66] is inapplicable at low MW, where the approximation of a thin interfacial layer, on which it is based, may not hold.

Table 2. The parameter β and the thicknesses of their interfacial layer Δ (at T = 293 K).

Primary structure	10^{-3} M/x_2, wt.%	P	SMS	Method	β	Δ, nm	Refs.
PS-PI	(21—102)/(0.39—0.60)	1.15	lamellae	SAXS	2/3	1.7—2.6	[67]
PS-PI	M_2:13—144/0.15	—	PCP, PI spheres	SAXS	2/3	1.8	[93]
PS-PI	M_1:93—232/0.25—0.80	1.20	variable	SAXS	—	2.9	[94]
PS-PI	8.5—205/0.50	1.22	lamellae	SAXS	0.79	<5.0	[62]
PS-PI	2.7—11/0.50	—	—	DSC	—	0.8—1.4	[13]
PS-PI			PI spheres		0.63		[93]
PS-PB	M_1:77—560, M_2:11—230/0.12—0.36	1.10	PB spheres, BCCP-paracryst.	SAXS	0.37	2.0—2	[91]
PS-PB	$M_1 = 80$, M_2=13/0.136	1.07	BCCP, PI spheres	SAXS	—	2.0	[92]
PS-PB	4—60/0.53—0.87	—	variable	EM, SAXS	0.58	—	[95]
PS-PB	$M_1 = 7$. $M_2 = 28$/0.75	—	PS spheres	SAXS	—	0.44	[53]
PS-PI-PS	M_1: 7.8; 14.5/0.85; 0.59	1.12	variable	SANS	—	2.9	[94]
PS-PI-PS	32.5—96/0.50	1.25	lamellae	SAXS	—	<5.0	[62]
PS-PB-PS	M_1 =7.8, M_2=43/0.75	—	PS spheres	SAXS	—	0.63	[53]
PI-PS-PI	59.9—134/0.50	1.30	lamellae	SAXS	—	<5.0	[62]

Notation: SANS = small-angle neutron scattering method; for the remaining notation, see the footnote to Table 1.

The experimental data compiled in Table 2 indicate the stepwise character of the variation of D in the experimental range of MW and an appreciable scatter of the results obtained by different workers. In the range of values of M from 2×10^4 to 2×10^5, the empirical relation $D = 0.024\ M^{2/3}$ has been obtained and is valid for di- and tri-BP[67] (it was assumed that $M_0 = M_A + \frac{1}{2}M_B$ for tri-BP of the ABA type). This relation agrees well with the theory developed by Semenov[37] and Zhulina and Birshtein[64,65] and somewhat less well with that of Helfand and Wasserman.[66]

(b) The Influence of the Molecular Weight Distribution

The studies on the symmetry and period of the SMS examined above refer to BP with a narrow MWD, which can be regarded as monodisperse to a first approximation. The influence of polydispersity on the period of the SMS has been studied theoretically.[34,40] A simple expression for the period has been obtained in the limiting case where the content of the type 1 component is low:[34]

$$D = (2\pi a/3)[3(r_{12}r_{1w} - 1)/2\bar{\nu}^2]^{1/6},$$

where $r_{12} = \overline{r^3}/\overline{r_1^2}$, $r_{1w} = \overline{r_1^2}/\overline{r_1}$, and $\bar{\nu}$ is the average number of neighbours per short block. For di-BP and tri-BP of type 1—2—1, the parameter $\bar{\nu} = 1$ and D is a maximum, while for tri-BP of type 2—1—2, $\bar{\nu} = 2$ and D is a minimum with $D_{max}/D_{min} = 2$. The period diminishes with increase in the number of blocks in polyblock copolymers.

A smooth increase in the period D with increase in the fraction of long chains in the blend of two di-BP having different block lengths but identical intramolecular contents of the components and with increase in the polydispersity coefficient in di-BP having a Schultz—Zimm distribution has been predicted.[40]¶

The influence of polydispersity on the SMS has been studied experimentally in blends of two monodisperse BP with identical intermolecular components differing in the MW or in the number of blocks.[69] If a tri-BP with a cylindrical SMS is added to a di-BP having a lamellar SMS, then, for a low content of the former, the lamellar structure persists, its parameters varying with composition. This indicates the compatibility of blocks of one kind. In the region of average compositions, two macroscopic phases coexist, each being a saturated solution of one BP in the other and the geometrical parameters of the microphases do not change on dissolution. For high contents of the tri-BP, only a cylindrical structure is formed, its parameters depending on the composition.

If a di-BP with a low MW, in which there is no ordered SMS, is added to a tri-BP having a lamellar SMS, then, for a di-BP content up to 50%, the lamellar structure persists, undergoing only a smooth change in its period, and then sudden disordering takes place. This makes it possible to assign this transition to first-order transitions. Studies have also established that the blending takes place at a molecular level and not at the level of the lamellae.[69] It is noteworthy that the components of the blend were not rigorously monodisperse and that the polydispersity varied with composition.

Analysis of experimental data on BP blends having a lamellar SMS[70] has led to the following observations. Since the number of thermodynamic components in such blends is two, macroscopic separation of the liquid—liquid type can occur in them. The parameter of the interaction of BP of type α with BP of type β is defined by the formula[71]

$$\chi_{\alpha\beta} = \chi_{12}(\Phi_{1\alpha} - \Phi_{1\beta})^2 = \chi_{12}(\Phi_{2\alpha} - \Phi_{2\beta})^2,$$

¶ It has been noted[40] that the study of Leibler and Benoit[68] proved to be erroneous because of the use in the latter of number-average molecular weights.

where $\Phi_{1\alpha}$ and $\Phi_{2\alpha}$ are the volume fractions of blocks of the first and second kinds in the BP of the α and β types and χ_{12} is the parameter of the interaction between the polymers 1 and 2. Since $\Phi_{1\alpha} = \Phi_{1\beta}$ and $\Phi_{2\alpha} = \Phi_{2\beta}$ in the blends investigated, it follows that $\chi_{\alpha\beta} \to 0$. Consequently, in the absence of microphase separation, there is also no macrophase separation, which can occur only as a consequence of the microlayer formation in one of the BP. A mixture of substances which are compatible in the melt but separate into layers on crystallisation is a low-molecular-weight analogue of the BP blend.

With decrease in temperature or on evaporation of the solvent, the block copolymer α having a higher MW and hence a higher T_{cr}^{micro} than the copolymer β is the first to begin undergoing a phase separation. The copolymer β then acts as a solvent, reducing T_{cr}^{micro}. Presumably the equilibrium structure comprises either a mixture of lamellar domains with periods D_α and D_β (structure I)[70] or of lamellar domains with a period D_{mix} and $D_\beta < D_{mix} < D_\alpha$ (structure II).[40,70] In the first case domains and in the second molecules have been mixed. It has been suggested that structure I is stable, while structure II is metastable, since the chains in the latter are perturbed to a greater extent the greater the difference between the sizes of the chains, which increases the free energy. Structures I and II have been observed respectively for large and small differences between the MW of the block copolymers α and β.

If the rate of the microphase separation is lower than the rate of the translational diffusion of the block copolymers α and β, then the microlayer formation in α leads immediately to phase separation between α and β. On further cooling, β also undergoes microphase separation, which leads to structure I. On the other hand, if the rate of microphase layer formation is lower than the rate of translational diffusion, then there is insufficient time for β to diffuse and structure II results. In a study[73] where structure II was observed, it was postulated that it can be both metastable and can correspond to equilibrium, provided that the MW of α and β do not differ greatly.

(c) The Influence of the Number of Intramolecular Components

Hitherto we have discussed two-component BP. However, from both theoretical and practical points of view, BP with three and more components are of interest. A large number of three-component BP have been synthesised and partly investigated[74–86] but the structure has been apparently studied only for PS–PVMA†–PI.[83] Each block of this BP is segregated in "its own" domain, which leads to a three-phase periodic structure. Overall, the SMS consists of alternating PS and PVMA lamellae, while the PI domains are distributed regularly within the PVMA lamellae, forming a two-dimensional structure (Fig.5d).

The field of study concerned with the SMS of BP with three and more components separated into microphases, the theoretical and experimental investigation of all possible types of symmetry of the SMS, and of the forms of the domains is of current interest; the MSB in them has not been investigated at all.

3. The Size of the Domains

The size of the domains should depend primarily on the MW of the blocks and their temperature. The influence of temperature has not so far been investigated either theoretically or experimentally.

† Poly(vinyl methacrylate) (Editor of Translation).

The influence of the MW has been studied only under conditions remote from the MSB, but the domains have a narrow interfacial layer. Theories concerned with the calculation of parameters of the micro-domain structure such as the size of the domains and the thickness of the interfacial layer as well as their dependence on the MW are based on the reasonable assumption of a thin interfacial layer. These theories predict the sizes of the domains in di- and triblock BP, postulating the symmetry of the SMS: cubic with spherical domains,[47] hexagonal with cylindrical domains,[87] and lamellar.[66] The size of the domains has been recently calculated from first principles.[37] A critical survey of the dependences of the size of the domains on MW for $\chi r \gg 2$, i.e. far from the MSB, has been published[70] for di-BP.

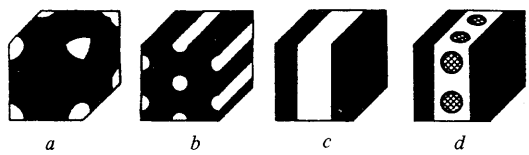


Figure 5. Types of symmetry of the ordered SMS of two- (a, b, and c) and three-component (type ABC) (d) BP:[18] (a) body-centred cubic packing of spheres of phase II in matrix of phase I; (b) hexagonal packing of cylinders of phase II in matrix of phase I; (c) alternating lamellae of phases I and II; (d) alternating lamellae of phases I (A blocks) and III (C blocks) with spherical domains of phase II (B blocks) within phase III.[83]

For spherical domains, the radius of the nucleus of the micelle in the ordered structure is described by the formula[37]

$$R = 2.18\, a r^{1/3} \Phi^{-1/3} \chi^{1/6}.$$

The predicted power dependence of R on the MW with a power exponent of 2/3 agrees with the dependence for lamellar domains,[64,65] the agreement with the conclusions reached by Helfand and Wasserman[66] is less satisfactory, and it differs markedly from the exponent 1/2 predicted by Meier.[96]

In a binary blend of binary BP with blocks having different MW, the thickness of the lamellae, formed by blocks of one kind mixed at the molecular level, is equal to the thickness of the lamellae formed in a BP having the number-average MW of the polymers α and β: $M_n = x_\alpha M_\alpha + x_\beta M_\beta$ (x_i is the number-average fraction of the polymer i). The power exponent in the relation between R and M_n is then 2/3.[70] Thus the size of the domains in BP blends is described by a power relation with the same exponent as in the pure BP. However, a different power exponent, namely 4/5, has also been obtained[69] for BP blends, so that it is necessary to revise these exponents taking into account the non-equilibrium nature of the SMS and the supercooling of the system relative to the MSB.

The degree of homogeneity of the lamellar domains with respect to size proved to be much greater than the homogeneity of the BP with respect to the MW. The degree of polydispersity with respect to the size of the domains is $D_w/D_n = 1.001$, whereas with respect to the MW it amounts to $M_w/M_n = 1.1$, which shows that the macromolecules are packed in domains and that the distribution of the latter with respect to size is much narrower than the MWD.[88]

It is noteworthy that structures with spherical and cylindrical domains have been less thoroughly investigated than the lamellar structures.

4. The Interfacial Layer

It is natural to suppose that, under conditions remote from the MSB, the thickness of the interfacial region is much smaller than the size of the domain. The theories developed in a number of studies[37,47,66,86,96] have been constructed on the basis of this hypothesis, which has been shown experimentally[105] to hold satisfactorily. These theories do not, however, yield an explicit analytical relation for the concentration profile of the block copolymer $\psi(r)$ in the form of a periodic function. We may note that for homopolymer blends, this relation has a form of the Kahn–Hilliard type:[102,103]

$$\psi(r) = \tanh(2r/a_1), \tag{2}$$

in which the thickness Δ of the interfacial layer can be defined as follows:

$$\Delta \equiv \left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\bigg|_{r=0}\right)^{-1} = a_1 = 2a_K/(6\chi)^{1/2} \tag{3}$$

where r is the distance from the interface and a_K the length of the Kuhn segment. Despite the fact that these expressions have been obtained for polymer blends, they have been frequently used also for the analysis of BP.

An expression for the concentration profile under conditions remote from the MSB, valid for lamellar BP and blends, has been obtained recently in an explicit form:[104]

$$\psi(r) = \frac{1-h}{2} F,$$

where $h(r) = k\,\mathrm{sn}(2r/a_1, k)$ is an elliptical Jacobi function with a modulus $k > 0$, a_1 the thickness of the interfacial layer specified by Eqn.(3), and F a complex function of elliptical integrals of the first and second kinds and of the Jacobi function which is independent of r. For $k \neq 1$, the function $h(r)$ is periodic with a period $4(2a_1)^{-1}D$, and, when $k = 1$, i.e. when $D \to \infty$, it is converted into the function (2).

To a first approximation, the thickness of the interface is

$$\Delta(k)/\Delta(1) = [1+2\varepsilon S_1(k)]/k, \tag{4}$$

where $S_1(k)$ is a function whose values lie in the range (0,1), which depends on χr, and ε is a small quantity. For blends, $\varepsilon = 0$ and $\Delta(1) = a_1$, i.e. Eqn.(3) is obtained. Block copolymers have a finite period ($k < 1$) and it follows from Eqn.(4) that they have a thicker interfacial layer.

The thickness of the interfacial layer under conditions remote from the MSB, measured in different studies (see Table 2, and also Henderson and Williams[98] and Shilov et al.[105]) is in the range from 4.4 to 30 Å. The scatter of its values is fairly large and may be associated both with the different ways of calculating the thicknesses from low-angle X-ray and neutron scattering data and with the non-equilibrium nature of the specimens. Various adjustable functions have been used[105] for the electron density profile, but the most realistic equation (4) has not so far been used for analysis.

The influence of this equilibrium on the thickness of the interface has been investigated in relation to BP with spherical domains.[106] The thickness of the interface in a specimen prepared under non-equilibrium conditions (at a temperature below the glass point of one of the components) and then heated above the glass point diminishes exponentially, tending to the limiting values 7.5 Å (the relaxation time is ~60 h). The diameter of the domains then changes little.

The equilibrium thickness determined from experiments on annealed specimens is more than twice smaller than the value calculated by Eqn.(3). The following possible causes of this discrepancy have been quoted:[106] (1) systematic errors in the calculation from low-angle X-ray scattering data to which the greatest contribution may come from the density fluctuations within the domains which has not been taken into account; (2) the inadequate accuracy of the determination of the quantities χ and a in Eqn.(3); (3) the unsuitability of Eqn.(3) at temperatures where one of the components has been converted into a glass. In our view, we may note yet another cause, namely the lack of validity of the application of Eqn.(3), obtained for blends, to BP.

Comparison of the thicknesses of the interfacial layer with the sizes of the domains shows that their ratio does not usually exceed 0.1, which indicates the validity of this intervening layer approximation under conditions remote from the MSB. Nevertheless, the volume fraction of the substance in the interfacial layer can reach considerable values (up to 30%).

Henderson and Williams[99,100] put forward and developed the hypothesis of the asymmetry of the concentration profile in the interface. However, since this hypothesis was based on the temperature variations of viscoelastic quantities, it may reflect the temperature asymmetry and not the spatial asymmetry. At any rate, the hypothesis requires experimental confirmation.

Hitherto we have considered the behaviour of the concentration profile under conditions remote from the MSB. The distribution of concentration in the form of a periodic profile has been obtained on the basis of Landau's theory near the consolute point:[107]

$$\psi(r) = \psi_m(t, k)\sin[r/\delta(t, k)], \tag{5}$$

which is similar to that illustrated in Fig.2. The parameters of this function are defined by the relation

$$\psi_m(t, k) = \psi_0[|t|k^2/(1+k^2)]^{1/2},$$
$$\delta(t, k) = \Delta_0[(1+k^2)/|t|]^{1/2},$$

where $t = T - T_{cr}$, while ψ_0 and Δ_0 are expressed in terms of the coefficients of the Landau expansion. The modulus k is determined by specifying the period $D = 4K(k)$, where $K(k)$ is the total elliptical integral of the first kind.

According to Eqn.(3), the thickness of the interfacial layer is given by

$$\Delta(k, t) = \Delta_0(1+k^2)/|t|k.$$

For a fixed period D, the amplitude of the profile $\psi_m(t) \propto |t|^{1/2}$ and the thickness $\Delta(t) \propto |t|^{-1}$ as the consolute point is approached. For a specified t, the increase in the period ($k \to 1$) converts Eqn.(5) into an expression analogous to Eqn.(2), while the decrease in the period ($k \to 0$) leads to the expression

$$\psi(r) = \psi_0 k|t|\sin(r/\delta).$$

The relation

$$\Delta(k)/\Delta_{min} = (1+k^2)/2k,$$

where $\Delta_{min} = 2\Delta_0|t|$ predicts an increase in the thickness of the interfacial layer with decrease in the period (on passing from a blend to the BP) and the amplitude ratio

$$\psi_m/\psi_m^{max} = [2k^2/(1+k^2)]^{1/2}$$

indicates a decrease in the miscibility of the components in the bulk of the phases on passing from the BP to the blend. This theory is applicable to the range of not unduly low MW of the blocks, which entails an increase in the upper consolute temperature (UCT) and hence is responsible for the difficulty of the experimental test.

The influence of temperature on the thickness of the interfacial layer has been investigated for BP in which the disappearance of the periodic SMS was observed.[50] An increase in temperature did not alter the thickness of the interfacial layer. Such qualitative discrepancy with the theory can be explained either by the fact that the composition differs from the critical composition or by the appearance of a cooperative surface instability (see above), which was not taken into account in the theory.

5. The Chain Conformations in the Domains

The interface should exclude some of the possible conformations of the block and the radius of inertia of the blocks should therefore differ from the radius of inertia of chains of the same length in the absence of an interface. So far only a small number of studies have been devoted to the elucidation of these differences and also of the degree of overlap of neighbouring coils. There are contradictions between ideas concerning the degree of interpenetration of coils of one kind in the direction normal to the surface of the lamella. Some workers conclude that there is slight interpenetration of the coils, so that double layers are produced (Fig.6),[62] while others conclude that they overlap to a marked extent.[70] In the direction parallel to the surface of the lamella, neighbouring coils overlap markedly[67] and are compressed. This compression is accompanied by the swelling of the coils along the normal to the surface, so that the overall radius of inertia remains virtually unchanged.[90]

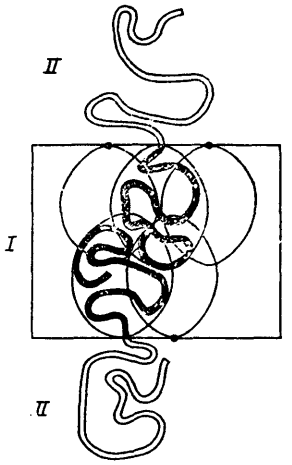


Figure 6. The relative disposition of coils of different blocks in a di-BP within the lamellae: (I) lamellae comprising type I blocks; (II) lamellae comprising type II blocks.

A change in the radius of inertia of the chains relative to the radius of inertia of the corresponding homopolymers have not been observed in the spherical domains.[91] The radius of the domains and their packing are then approximately the same as predicted by Vallance and Cooper.[86] Under non-equilibrium conditions, which frequently obtain in BP with a high MW obtained from a solvent, the macromolecules have significantly greater radii of inertia and the size of the domains at high BP concentrations and/or low temperatures diminishes in accordance with the law $D \propto \Phi_{BP}^{-\gamma}$, where γ = 1/3 for spherical domains, 1/2 for cylindrical domains, and 1 for lamellae.

The average area of the interface per chain (between neighbouring chemical cross-links joining the blocks along the interface), S/N, where N is the number of chains passing through the interface, is described by the following empirical scaling law for both narrowly dispersed BP and their blends:

$$S/N \propto M_n^{1-\beta}, \tag{6}$$

where the exponent β = 2/3. We may note that, among all the types of average molecular weights (M_n, M_w, M_z), M_n leads to the best adjustment of the relation. A relation of type (6) with an exponent of 1/3 is applicable to both lamellar[70] and spherical[91] domains.

6. The Grain Size

An ordered inter-domain structure is limited by the grain size, which is of the order of several microns. The grain boundaries are two-dimensional defects analogous to the boundaries of a crystallite in polycrystalline substances and of magnetic or electrical domains in ferromagnetic and ferroelectric materials. Rod-shaped grains have been observed in BP with lamellar and cylindrical domains, the grains being distributed at random relative to one another.[110,111] These anisotropic grains are strained and are surrounded by cavities and inclusions. It has been suggested that the stresses arise during the evaporation of the solvent.

The optical axis of the grain is parallel to the axis of the cylindrical domains and can be directed either parallel or at an angle to the axis of the rod-shaped grain. Single supercrystals exhibit double refraction associated with the difference between the refractive indices of the microphases.[112,113] If the optical axis is at an angle to the rod, then, on heating, it becomes parallel to the latter owing to the relaxation of the elastomer phase and the rotation of the cylinders.[112] The size and shape of the grains have been investigated by the low-angle scattering of depolarised light, which depends on the anisotropy of the shape and boundaries of the grains.[110,114] The domains do not contribute to the scattering, since their size (300 to 500 Å) is much smaller than the wavelength. The scattering by mechanical stresses is negligible. Apart from the defects of the type of grain boundaries, defects of the type of dislocations have also been observed.

Using special methods, it is possible to obtain macroscopically anisotropic specimens,[21] which are sometimes called single supercrystals by analogy with single crystals. There exist three methods for obtaining them: (1) by the shear flow of the melt,[21,115] (2) by extrusion,[116] and (3) by casting from a solution with a high boiling point of the solvent.[117]

7. Kinetics of Microlayer Formation

The kinetics of separation into microphases (in the abrupt transition from the single-phase state to the region where two-phase states are stable) in BP should be in general analogous to the kinetics of

the separation into macrophase layers in mixtures, although it should have its characteristic features. However, despite the vigorous studies on the kinetics of separation of blends (as regards homopolymer blends, see, for example, Refs.118–131), the separation of BP melts into layers has been little investigated.

The early stages of the spinodal decomposition have been investigated theoretically in a study[34] where it was shown that periodic (with a period $L_0 = 2\pi/k_0$) inhomogeneities form a train with a length l ($l \gg L_0$), which increases in accordance with the diffusion law

$$l^2(t) \propto l_0^2(t)/\tau(k_0, \Delta T),$$

where l_0 is the length of the train under the conditions of slight supercooling, while the amplitude of the inhomogeneity increases exponentially. The period L approaches L_0 after a time. These theoretical predictions have not so far been confirmed experimentally.

The experimental study of the kinetics of the appearance of the structure is complicated by the need to use powerful sources of X-ray (including synchrotron) radiation or neutron radiation, which make it possible to reduce significantly the exposure time.

There exists the possibility, in principle, of studying the kinetics of microlayer formation by simpler methods, when the components are capable of vitrifying. Such systems can be quenched at various stages of the phase separation and a change in the phase state can be investigated from vitrification parameters, which depend on the amplitude and size of the fluctuations. The increase in the heat capacity jump on vitrification with increase in the phase separation time has been observed by this method.[10,24] In the first instant, there was no jump, which is most probably due to the large scatter of the period and the low amplitudes of the fluctuations. After the appearance of the jump, its width changes insignificantly, which shows that fluctuations with a small scatter of the period contribute to the vitrification jump. The heat capacity jump, corresponding to the second phase, has not been observed either because of the small amount of the phase (it has not been recorded also in the phase separation of blends of homopolymers)[131] or owing to the small size of the phase (it has been shown[163] that, when the size of the particles of the phase is less than 60–70 Å, its vitrification is not recorded). However, in other experiments cooling in the postulated single-phase state leads to the observation of the two vitrifications, although one of them is highly diffuse.[51]

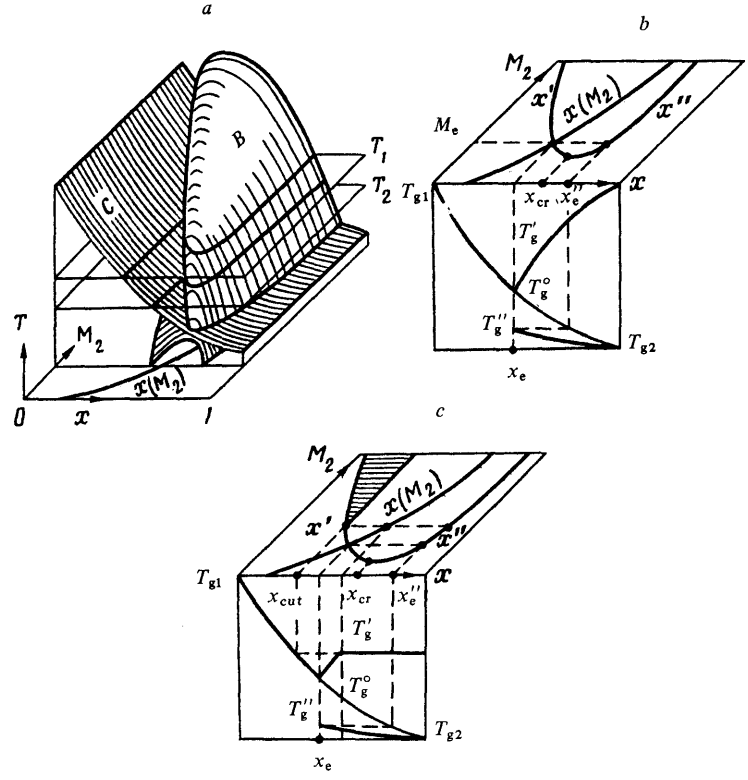


Figure 7. Construction of the vitrification diagrams for BP with M_1 = const. by the surface intersection method:[10] (a) three-dimensional representation of the surfaces in terms of the coordinates $T-x-M_2$ [B— binodal surface; C— vitrification surface for a single phase system (VSSS); $x(M_2)$—overall composition curve; T_1 and T_2—planes corresponding to the temperatures T_1 and T_2]; (b) section through the surfaces by the T_1 plane and the corresponding VD (x' and x''—compositions of the coexisting phases; x_{cr}—critical composition; x_e, M_e—the point at which the composition curve enters the region under the binodal surface; x_e''—the composition of the second phase at the point of entry; T_{g1} and T_{g2}—glass points of the pure components; T_g^0—VCSS; T_g' and T_g''—glass points of phases I and II respectively); (c) section through the surfaces by the T_2 plane ($T_2 < T_1$) and the VD corresponding to the section (x_{cut}—cut-off composition).

The kinetics of the disappearance of the SMS after a sharp increase in temperature have been investigated for PS–BP di-BP with $M_n = 5.2 \times 10^4$ and $\chi_{PS} = 0.30$ (to reduce the temperature of the transition to the BP, 60% of solvent was introduced).[132,133] Microdissolution occurred rapidly (after ~30 s) and accelerated on raising the final temperature. The scattering curve in the final stage corresponded to scattering by a homogeneous BP melt with a broad and weak maximum due to the effect of the correlation hole.

III. MUTUAL INFLUENCE OF MICROLAYER AND GLASS FORMATION

Separation into microlayers and glass formation exert a mutual influence on one another. On the one hand, microlayer formation determines the vitrification of the system if the phase state of the material does not change on cooling to the vitreous state. On the other hand, vitrification can be influenced in microlayer formation if during its occurrence one of the phases can vitrify, which leads to the deviation of the phase state from equilibrium.

The vitrification of BP is determined by parameters of the concentration profile (in the more general case, the density profile) such as the amplitude of the profile, the size of the domains, and the width of the intermediate layer. For different coefficients of the thermal expansion of the phases, the SMS should play a role. The commonest method of investigation of vitrification involves the construction of plots of T_g against the MW of a fixed composition or the construction of plots of T_g against composition for a fixed length of one of the blocks (usually the rigid block, i.e. one with a higher glass point T_{g1}). In relations of this kind, not one but several of the above parameters of the concentration profile contribute to T_g. The estimation of the contributions of different parameters requires special consideration in each case. The direct problem involves in this instance the study of vitrification in systems with a known concentration profile and is still at the beginning of its solution. The converse problem is usually solved: conclusions concerning the different parameters of the profile are reached from the vitrification investigated.

1. Vitrification in Block Copolymers which have Undergone Microphase Separation at Temperatures above the Glass Points of the Components

We shall assume that the systems have a binodal curve with a UCT which lies above the T_g of both components. On transition of the system from the single-phase state to the region of stable two-phase states, at temperatures above the T_g of both components, vitrification does not influence the phase separation and the system can, in principle, reach the state of equilibrium. Subsequent quenching from the phase separation temperature (annealing temperature) freezes (as a consequence of vitrification) the structure of the liquid corrsponding to a definite temperature. By quenching the melt from a specific point in the phase diagram, it is possible to compare the vitrification parameters at the given point on the $T-x$ phase diagram.

(a) Vitrification Diagrams (VD)

As already mentioned, the influence of phase composition on the temperatures of the transitions to the BP can be conveniently represented in terms of the $T-x-M_2$ variables for a fixed M_1. We shall consider initially the behaviour of the glass points on varying the composition of the BP annealed at a temperature T_1 (to which corresponds the T_1 plane in Fig.7a). Before the composition curve enters the region underneath the binodal surface, the system remains in the single-phase state and its single glass point should obey the relations characteristic of T_g for single-phase systems comprising two components. The glass point T_g in this composition range may be described by different semiempirical formulae obtained for SP and homopolymer blends,[135–138] which are also suitable for single-phase BP.[139]

When the composition curve enters the region under the binodal surface, a second phase appears, to which corresponds a second glass point. Depending on whether the composition curve enters from the left or from the right relative to the consolute point, either low-temperature or high-temperature vitrification will occur abruptly on the T_g–composition diagram (VD) (Fig.7b). On further increase in the length of the flexible component, the glass points of both phases should move away from one another, since the separation range $x''-x'$ increases. For this reason, a dip should be observed in the upper branch, whose minimum should be located at the point corresponding to the onset of phase separation. The first and second derivatives should change abruptly at this point.[10,24] For very large lengths of the flexible blocks, the composition curve can emerge from the region underneath the binodal surface and the upper T_g' branch then terminates.

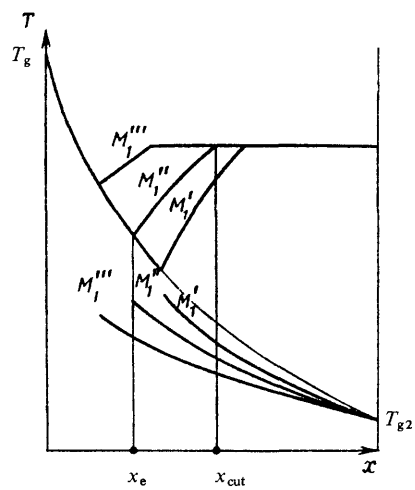


Figure 8. The influence of M_1 on the form of the vitrification diagram (the increase in the number of primes in the designations of the curves denotes an increase in M_1); x_{cut}—cut-off composition; x—content of the second component.[10]

With decrease in the phase separation temperature, the branches on the VD should move apart and the bifurcation point should shift towards lower contents of the flexible component. The increase in M_1 for a fixed phase separation temperature is analogous to a decrease in temperature for a fixed M_1 (Fig.8).

The type of VD predicted by the methods of topological thermodynamics has been observed experimentally for polyblock[39,84,140] (Figs.9a and 9b) and di- and tri-block[141] (Fig.9c) BP. For a low

content of the flexible component, a single vitrification is observed and the T_g of the BP varies in accordance with the same law as that governing SP (this has been tested both by measurements on SP and by calculations using the corresponding formulae). Thus, in the above composition region, the BP considered can be regarded as single-phase. The decrease in T_g depends not only on the content of the flexible component but also on the MW and the primary structure of the BP (di- or tri-block or star-shaped).[141] In BP with specific intermolecular bonds, an increase in M_1 for the same composition entails a decrease in T_g.[39,140] The decrease in T_g to the MSB amounts to several tens of degrees according to some data[141] and reaches 130 K according to others.[140]

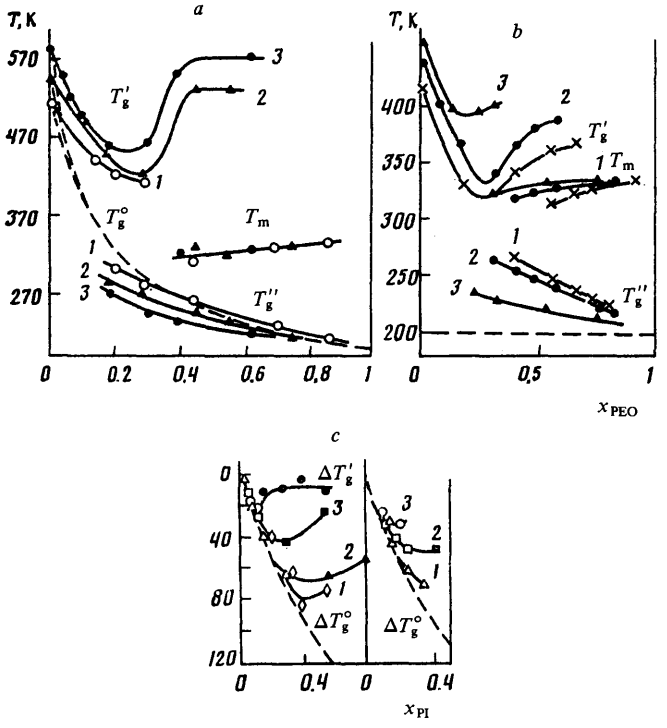


Figure 9. Experimental vitrification diagrams for BP (the increase in the number of the curve corresponds to an increase in M_1): (a) $(PA-PEO)_n$[39] (T_m—melting point); (b) $(PASO-PEO)_n$;[84] (c) PS–PI (on the left), PS–PI–PS (on the right);[141] $\Delta T_g' = T_{g1} - T_g'$; $\Delta T_g^0 = T_{g1} - T_g^0$ (the open and filled symbols denote single-phase and two-phase states respectively); x—the weight content of the component with a low glass point.

The second region—the region before the onset of phase separation—is characterised by a deviation of T_g' from the T_g of SP and by the appearance of a second transition to a vitreous state (T_g''). In some cases, the onset of the deviation coincides approximately with the appearance of the second transition,[39,84] while in others the second transition appears after the start of the deviation.[141,143] An attempt has been made to explain the latter finding by the presence of a large fraction of interfacial layers, which is unlikely. The increments in the compositions of the components were not always sufficiently small. For this reason, one cannot determine exactly the start of the appearance of the second vitrification and the form of the dip in the upper branch, although there is no doubt about the existence of the dip. A decrease in M_1 shifts the MSB towards higher values of x and increases the depth of the dip in the upper branch, which is consistent with the predictions by the geometrical method. The width of the heat capacity jump then increases.[141] After its abrupt appearance, the temperature T_g'' initially differs markedly from T_{g2}, but approaches the latter as x increases. We may note that for the BP discussed, the vitrification curve for single-phase systems (VCSS) is concave and for this reason the addition of the rigid component to the phase with a high content of the flexible component results in an appreciably smaller change in the T_g for the phase than the introduction of the same amount of the flexible component into the rigid phase. It is therefore difficult to observe the deviation of T_g'' from T_{g2}.

In the third region (with a high content of the flexible component), two T_g, differing from T_g^0, are observed, which indicates the existence of two amorphous phases. In this composition region, T_g' either approaches T_g for the corresponding homopolymers[39,141] or reaches a limiting value without attaining T_{g1}.[84] In the latter case, microphase separation is apparently inhibited by the vitrification of the rigid phase (cf. subsection 2 below).

The close correspondence between the forms of the VD predicted by the method of topological thermodynamics, which is based on the hypothesis that T_g depends solely on the phase composition, and the experimental VD as well as the large difference $T_g' - T_{g1}$ (up to 130 K) permit the conclusion that the change in the glass points of the BP indicated is responsible for the change in the amplitudes of the concentration profile as the composition is varied. The behaviour of T_g on crossing the MSB has been explained[141] by the presence of a large fraction of the interfacial layer, which appears to be inadequately justified.

(b) Vitrification in the Two-Phase Region in the Vicinity of the MSB

In the experimental studies examined above, the composition and MW ranges investigated included the MSB. The behaviour of the glass point as the microlayer formation boundary is approached from the side of the two-phase region has not been more thoroughly investigated, although the proximity to the boundary is not always clear because the position of the boundary itself is frequently unknown. It has been noted in many cases that, as the MSB is approached by reducing the MW of the blocks, T_g' falls and T_g'' increases (Table 3). Under these conditions, T_g' diminishes faster than T_g for the corresponding homopolymer. Extrapolation of T_g' and T_g'' to di-BP[108] and poly-BP[104] for a constant composition (decrease in the MW of the blocks in the former case and with increase in the number of blocks, keeping the overall MW constant, in the latter) leads to the intersection of the branches at the point which coincides with the T_g for the SP having the same composition.

Although the fact that the glass points approach one another is not open to doubt, there is as yet no unambiguous explanation for it. This is because the decrease in the MW of the block entails a decrease in the size of the domain and can lead simultaneously to a change in the phase composition and in the thickness of the interfacial layer and also in the MSB. The displacement of T_g is therefore attributed to a series of phenomena: (1) the increase in the content of the interfacial regions;[141,144,145] (2) the increase in the surface/volume ratio owing to the change in the SMS;[153] (3) the

intensification of the dynamic interaction of the flexible and rigid blocks which leads to joint segmental motion;[108] (4) the effect of interfacial tension between the microphases;[161,162] (5) the increase in the average free volume of the vitreous phase under the influence of the mixing near the interface;[153] (6) the change in phase composition.[39,84] We believe that the mechanisms (3) and (6) are the most probable.

In the study of vitrification and of the influence on the latter of the parameters of the concentration profile, it is essential to know the phase state of the melt, since BP are frequently obtained by cooling the melt, which is accompanied by the freezing of its structure. In most studies on vitrification in BP, the phase state of the melt at temperatures above T_{g1} remained unknown. The investigation[134] in which the transition of the BP, tentatively from a two-phase state to a single-phase state,[49] was observed from the change in the viscosity of the melt and electron microscope data is important for this reason. After annealing above the temperature of the postulated transition to the single-phase state and subsequent quenching, very diffuse vitrification of the rigid phase is observed, so that it proved impossible to determine where this process begins. On the other hand, the vitrification of the flexible phase occurred at the same temperature as in the slowly cooled specimens. The values of ΔC_{p1} and the width of the vitrification range of the rigid phase decrease with decrease in the cooling rate, although the heat capacity jump remains more than a factor of two greater than in the corresponding homopolymer. These data apparently indicate a higher content of the flexible sigments in the rigid phase, although, despite the higher degree of mixing, the BP nevertheless remain in the two-phase state after annealing above the transition temperature and subsequent quenching. The existence of a two-phase structure can be associated both with the higher rate of layer formation on cooling in the single-phase state and with the existence of a microheterogeneity at temperatures above the rheological transition temperature (see the discussion of the cooperative capillary instability of the SMS with retention of the two-phase structure in subsection 2 of Section I above). Nor can one rule out also that the diffuse nature of the vitrification is associated with the influence of vitrification on the phase separation (see below).

(c) Vitrification in the Far Two-Phase Region

Apart from the increase in T_g'' with increase in the length of the flexible block, its decrease has also been observed in the two-phase region[155–160] (Table 3). Depending on the nature of the blocks, the decrements in the glass point $T_g'' = T_g'' - T_g^{homo}$ reached 19 K,[155] 15 K,[158] 13 K,[156,157] and 10 K.[160,161] The study of the SMS showed that such decrease is observed only for compositions such that the flexible phase constitutes closed inclusions in a vitreous matrix.[155,157] This led to the reasonable conclusion that the decrease in T_g'' is associated with the difference between the thermal expansion coefficients of the inclusions and the matrix. As a result of the covalent bonds between the flexible chains and the skeleton, the volume of the flexible inclusions cannot diminish on cooling the melt to the extent that they would have decreased in the absence of the skeleton (matrix). This should lead to a "negative pressure", extending the flexible domain. Estimates carried out for a spherical BP domain within a PS matrix from the formula[155]

$$\sigma_i = 2(\alpha_i - \alpha_m)E_iE_m\Delta T/[6E_m(1-2\mu_i) + 3E_i(1-\mu_m)]$$

Table 3. The behaviour of the glass points of the block copolymers when the parameters of the primary structure of the macromolecule are varied.

No.	Primary structure	Type of relation plotted	Position relative to the MSB	SMS	Character of variation of T_g	Method of study	Refs.
1	$(PA-PEO)_n$	$T_g(x)$, $T_g(M_2)$, M_1 = const	on either side	variable	Fig.9*a*	DSC	[39]
2	$(PASO-PEO)_n$	$T_g(x)$, M_1 = const	ditto		Fig.9*b*	DSC	[84]
3	PS-PI, PS-PI-PS	$T_g(x)$, M_1 = const	»	*	Fig.9*c*	DSC	[141]
4	$(PTMP-PDMS)_n$	$T_g(M_1)$, x = const	»	*	merging of T_g' and T_g'' with decrease in M_1	DMA	[147]
5	PS-PI	$T_g(M_1)$, $x = 0.5$	in two-phase region	lamellae	mutual approach of T_g' and T_g'' with decrease in M_1	DSC, NMR	[108]
6	PS-PB, PS-PI, PS-PEO	$T_g'(M_1)$	ditto	*	ditto	DSC	[150—152]
7	$(PS-PB)_n$, PS-PB-PS	$T_g(n)$, x, M_0 = const	»	lamellae	mutual approach of T_g' and T_g'' with increase in n	DMA	[144]
8	PS-PB-PS, PB-PS-PB, PS-PI-PS	$T_g(M_1)$, x = const	»	»	mutual approach of T_g' and T_g'' with decrease in M_1	DMA	[145]
9	PS-PDMS	$T_g'(M_1)$, $T_g(M_2)$	»	variable	ditto	DSC	[148, 149]
10	PS-PMS, PMS-PS-PMS, PS latexes		in remote two-phase region	*	T_g' and T_g'' remain unchanged	DSC	[154]
11	PS-PB, PS-PB + homo-PS	$T_g''(M_0)$, $T_g''(R_{sph})$	in two-phase region	variable	T_g'' decreases on formation of spherical domains	DMA	[155]
12	$(PCUS-PDMS)_n$	T_g''	ditto	*	decrease in T_g''	DMA	[156, 157]
13	PC-PDMS	$T_g''(M_1)$	ditto	*	decrease in T_g''	DMA	[164]
14	PPSO-PDMS	$T_g''(x_2)$, M_1 = const	»	variable	decrease in T_g'' with decrease in x_2	DSC	[158]

Notation. PA = polyarylate, PASO = poly(arylene sulphoxide), PDMS = polydimethylsiloxane, PMS = polymethylstyrene, PC = polycarbonate, PCUS = polycarbonate with terminal urethane groups, PPSO = polyphenylsilsesquioxane, and PTMP = polytetramethyl-*p*-silphenylenesiloxane.

* The supermolecular structure was not investigated.

(subscript i refers to the inclusion and m to the matrix; σ_i is the thermal stress developed within the highly elastic domain, α the thermal expansion coefficient, E the modulus of elongation, and μ the Poisson coefficient) lead to a negative pressure of 78 MPa. The decrease in T_g, calculated from the relation $dT_g/dp = 0.24$ K MPa^{-1} and equal to 18.7 K, agrees well with the experimental value.

After a time, the free volume should be lost from the inclusion as a result of the relaxation of the vitreous matrix (the compaction of the specimen), which diminishes the hydrostatic extension of the flexible inclusion with which the observed decrease $\Delta T_g''$ is apparently associated. However, one should note that thermal stresses should apparently act not only on the spherical flexible domains but also always when the rigid phase forms a monoconnected region, i.e. the matrix. In particular, they should act also on cylindrical flexible domains. It may be that a decrease in T_g'', which begins already when the content of the rigid block is $\sim 50\%$, is associated with this factor.[156,158] The relaxation time of the free volume owing to the rearrangement of the matrix should decrease with increase in the content of the flexible block.

It is remarkable that T_g'' depends on the MW of the flexible block and not on the size of the domains, the decrease in MW resulting in a fall of $\Delta T_g''$.[155] Although this has been explained[155] by the decomposition of the flexible blocks, which tends to lower the thermal strain, this hypothesis requires proof.

Generally speaking, thermal stresses should alter T_g'' not only far from the phase separation boundary (where a rigid matrix still persists) but also in its vicinity, provided that the composition curve enters the region under the binodal surface far from the consolute point. The phase compositions and hence the thermal expansion coefficients will then differ greatly, which will lead to an effect by the rigid matrix on the flexible inclusions.

The behaviour of T_g'' in the remote two-phase region permits the following conclusions. The identity of T_g'' for the BP with a long rigid block and T_g'' for the homopolymer having the same MW in the range of MW where T_g of the homopolymer still depends on the MW is not consistent with the concept of the free volume of the terminal units, since the free volumes of the BP and the homopolymer should differ significantly.[148,155,164] This permitted the logical hypothesis[164] that the flexible segments attached to the end of the rigid block are so mobile that they can transmit their mobility to the rigid block, which should thus behave as if it had a free end. This idea agrees with the conclusion[108] that the disposition of the rigid block in the tri-BP macromolecule (at the centre or at the ends) does not influence T_g.[108,152] However, we may note that, in contrast to Kanbur's study,[164] where the decrease in M_2 for x = const. did not alter T_g', the decrease in M_2 from M_1 = const. in the study of Levin et al.[157] lead to a decrease in T_g'.

Comparison of the behaviour of T_g' in a series of BP, where the rigid block was the same and different components were selected as the flexible block, showed that, at a remove from the phase separation boundary, T_g' is independent of the chemical nature of the flexible block and of the BP composition.[148-152] The chemical nature and the MW of the flexible block influenced T_g' only when the MW and the composition were close to the MSB.[152] From this, one may conclude that, since the compatibility of different oligomers with the rigid oligomer varies, under conditions remote from the phase separation boundary there is no blending whatever of unlike segments in the vitreous microphase.

The width of the jumps in the BP thermal conductivity is greater than for the corresponding homopolymers and only the upper part of the vitrification region with T_g'' broadens in the direction of higher temperatures (up to 32 K) and only the lower part of the vitrification region with T_g' broadens towards lower temperatures (down to 26 K). A decrease in the content of the rigid block, accompanied by a decrease in the size of the inclusions of the rigid phase, led to the broadening of the vitrification region on the low-temperature side as far as 43 K.[154] The width of the vitrification region of the flexible phase as a function of the specific surface of the interface fits on a single curve for all the systems investigated regardless of the nature of the interface (i.e. for both BP and latexes), which has led to the conclusion that the width is determined solely by the area of the interface. The widening becomes appreciable for a specific surface of $\sim 10^4$ m^2 kg^{-1}, which corresponds to a microphase whose size is 0.5 μm. From this it follows, in particular, that in homogeneous BP the vitrification range should be the same as in homopolymers. It has been suggested[154] that an increase in the temperature of the upper boundary of the vitrification region is caused by the fact that the two vitreous phases are separated by a solid interface. It was not appropriate to take into consideration the thickness of the interfacial layer, which should be very small in the remote two-phase region, for the explanation of the broadening of the vitrification region.

Thus the above analysis of the data and ideas available at the present time on the vitrification of BP undergoing microphase separation at temperatures above T_{g1} permit the following conclusions. In the region of the single-phase state, T_g obeys the relations valid for SP. In the region of the transition through the MSB, the glass point of one of the phases deviates from the relation describing SP and a second transition to a vitreous state appears. In the two-phase region near MSB, the T_g of the rigid phase is usually below the T_g of the corresponding homopolymer and the T_g of the flexible phase is above it. Both these effects can be explained either by an increase in the similarity of the phase compositions as the phase separation boundary is approached or by the dynamic interaction of the linked blocks. As the boundary is approached, $\Delta C_p'$ decreases while $\Delta C_p''$ increases, the width of the vitrification region in the rigid phase increasing. However, the treatment of the changes in the intensity and width of the transitions is not unambiguous and requires further study.

In the remote two-phase region, both glass points agree with the T_g of the corresponding homopolymers and the heat capacity jumps correspond to the contents of the components, but the width of the jumps is as a rule greater than for the homopolymers. The widening of the range corresponding to the low-temperature vitrification is directed towards higher temperatures, while the corresponding widening of the high-temperature vitrification is directed towards lower temperatures. This can be explained by the presence of an interface, the widening becoming more pronounced with increase in the specific area of the interface. It may be that this effect contributes also to the widening in the region of the MSB. In the composition range where the flexible phase represents a polyconnected region, a decrease in the T_g of the flexible phase compared with the corresponding homopolymer is observed. This decrease is associated with the stretching hydrostatic pressure, which is exerted by the rigid matrix on the domains comprising flexible covalently bound chains and is associated with the difference between the thermal expansion coefficients of the domain and the matrix.

It appears essential at the present time to investigate quantitatively the vitrification in BP whose phase state and SMS have been characterised not only in the region between the glass points of the components but also in the melt. The study of the vitrification in

the region of MSB taking into account the kinetics of phase separation appears especially important. Furthermore, it is essential to devise a theory of the vitrification of BP in all the regions of the phase diagram.

2. Vitrification in Block Copolymers Undergoing Microlayer Separation at Temperatures between the T_g of the Components (the Influence of Vitrification on Microlayer Formation)

If the phase separation temperature is below the boundary temperature T_b, determined by the intersection of binodal curve with the VCSS (Fig.10), then the fluctuation concentrations develop until their amplitude in the half-period with a large content of the rigid component reaches the cut-off value x_{cut} at which the glass point for this half-period, having increased, becomes equal to the phase separation temperature.[10,24] Thus the microphase with a high content of the rigid component passes to the vitreous state before the attainment of equilibrium as regards composition. This effect should shorten the separation range in the phase diagram and in the VD.

The influence of vitrification on the phase separation has been observed experimentally.[10,24] After the system has passed from the single-phase to the two-phase region, the thermogram does not show initially any anomalies. This is apparently associated with the fact that in the initial instant there are only smooth concentration fluctuations with a large scatter of periods, which leads to the pronounced spreading of the transition to the vitreous state. A small thermal conductivity jump then appears and grows as a function of time, while the temperature corresponding to the point of inflection (T_g) increases monotonically (Fig.11). With decrease in the phase separation temperature (T_{ps}), the glass point, determined after annealing for 1 h, decreases linearly by more than 100 K with a slope close to unity, which corresponds to the predictions of the geometrical method. No other factor, apart from the change in the phase composition can apparently shift T_g by more than 100 K. The analogy between the freezing of the phase separation as a result of vitrification and the self-inhibition of the hardening reaction of network polymers is noteworthy.

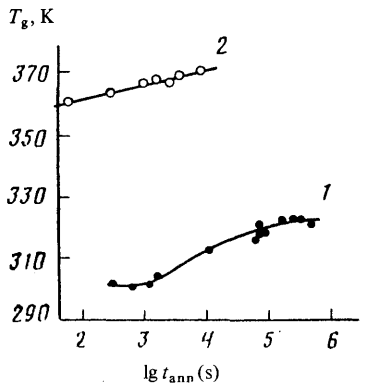


Figure 11. Dependence of T_g' on the annealing time in the PA–PEO BP:[10] (1) T_{ann} = 290 K; T_{ann} = 350 K.

The geometrical analysis based on the consideration of the intersections of the binodal surface, the vitrification surface for a single phase system (VSSS), and the temperature plane (T-plane), permits the construction of all possible types of T_g–composition and T_g–MW relations in the BP in the case where vitrification influences the phase separation.[10,24] This analysis presupposes that T_g depends solely on the phase composition. As an example, Fig.7a illustrates the mutual intersection of the binodal surface, the VSSS, and the T-plane. So long as the composition curve does not intersect the curve of the coexisting compositions, the system remains in the single-phase state. In this region, T_g should vary in accordance with the law for a single-phase system. If the composition x_c at which the composition curve joins the coexisting phases curve is greater than x_{cut}, then, after the start of phase separation, the difference between the phase compositions will increase and the glass points will therefore diverge. However, as soon as the composition of the phase with a high content of the rigid component reaches x_{cut}, it ceases to change on further alteration of the overall composition.

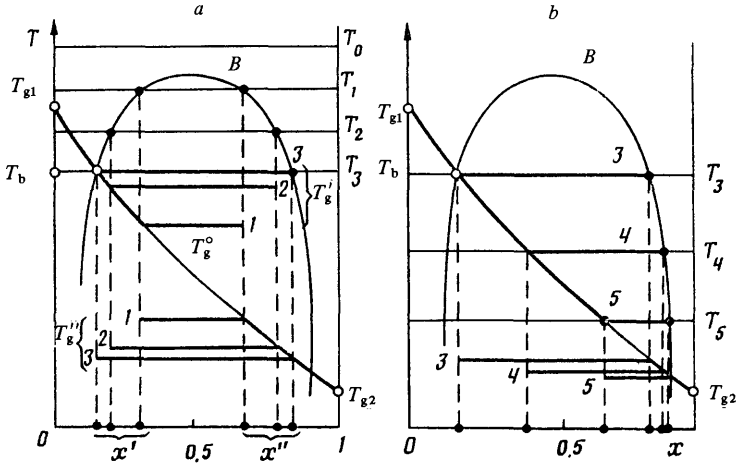


Figure 10. Construction of VD for blends in the case where the binodal curve and the VCSS are superimposed.[10] B—binodal curve; T_g^0—VCSS; T_b—boundary temperature; x' and x''—compositions of the coexisting phases; the numbers of the VD branches correspond to the subscripts of the T_i: (a) $T_i > T_b$; (b) $T_i < T_b$.

The upper branch in the VD beyond the cut-off composition should become horizontal (Fig.7).

The decrease in T_{ps} should reduce x_e and should increase x_{cut}, as a result of which the bifurcation point in the VD should shift towards lower values of x and and the horizontal plateau should be displaced towards lower temperatures. When the temperature falls so much that x_e becomes smaller or equal to x_{cut}, the bifurcation point should shift towards higher values of x and the dip in the upper branch should disappear. The plateau should again be displaced downwards as a linear function of T_{ps}. The increase in M_1 influences the form of the BP analogously to the decrease in temperature. All the possible forms of the VD, reflecting the influence of vitrification on the phase separation in BP, have been published.[10] VD, whose form is analogous to those discussed above, have been observed experimentally.[39,84,140,141] The attainment of a plateau below T_{g1} has been established most reliably by Godovskii et al.[84]

The above discussion shows that in the two-phase region, T_g for the rigid phase can be reduced owing to the presence of an excess of the flexible component in this phase. Since in the study of vitrification the BP was heated only slightly above T_{g1} in the vast majority of instances, the difference between the non-equilibrium and equilibrium compositions should diminish with increase in M_1 because the UCT then shifts towards higher temperatures and the equilibrium compositions approach the vertical axes. The decrease in T_g' with decrease in M_1 is apparently associated with this factor.

The study of the superposition of the layer formation and vitrification processes in BP and polymer blends has only just begun and detailed investigation of this problem is needed because such superposition is frequently encountered in practice.

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The above discussion on the microlayer and glass formation in block copolymers shows that in real systems these processes frequently superimpose and influence one another. For this reason, not only a detailed investigation of each separately but also of their mutual superposition and influence is needed. Despite the evident advances in the study of the mechanism of microlayer formation, we are still at the beginning of the path leading to the investigation of processes leading to microheterogeneity in BP. The influence of the MWD and of the number of blocks on microlayer formation, the microlayer formation kinetics, the transitions from one SMS to another, and the superposition of microlayer formation and vitrification have been studied inadequately. The importance of this field follows from the prospect that BP may be employed for technical purposes and also from the fact that BP constitute the simplest synthetic heteropolymers with a more or less ordered primary structure and serve as the first support of the bridge connecting synthetic and biological polymers. Specific synthesis of heteropolymers with an ordered primary structure will undoubtedly lead in the future to the complete construction of this bridge. The phase and microphase transformations in biological objects, which are multicomponent mixtures of heteropolymers and low-molecular-weight substances from the molecular point of view, apparently play an important role in the existence and evolution of living organisms.

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Specific Pyrolysis of Polycondensation Polymers

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The review discusses processes involving the thermochemical conversion of polymeric materials with a network structure (furfural and phenol-formaldehyde polymers) and polyimides into carbonaceous materials. The structural characteristics and properties of the carbonaceous materials based on the polymers are analysed and their applications are indicated. The bibliography includes 122 references.

CONTENTS

I. Introduction 999
II. The formation of the structures of carbonaceous materials on the basis of network polymers 999
III. Specific pyrolysis of polyimides 1003

I. INTRODUCTION

The successful development of modern technology is to a large extent determined by the creation of materials capable of retaining their operating properties at a high level under extreme conditions. The aromatic polyamides, polyimides, polysulphones, and polybenzoxazoles synthesised hitherto, in which a high thermal stability and heat resistance are combined with effective strength and dielectric parameters and with radiation and chemical stability, have made it possible to solve many problems in modern technology.

However, the possibilities of thermostable polymers are limited, the temperature of their prolonged use in air does not exceed 300 to 400° in most cases, and treatment with strong chemical agents can lead to their dissolution or decomposition. A further increase in the resistance of polymeric materials to the effect of temperature in corrosive media is possible by creating on their basis secondary carbon structures. Such structures are chemically inert, are highly resistant to heating, and in many cases possess a high mechanical strength. They are obtained by the heat treatment of macromolecular compounds under non-oxidative conditions.

The main type of polymers used to prepare carbonaceous materials comprises phenolic polymers in view of their low cost, large-scale production, and the reliability of the sources of the natural raw material. However, the relatively low yield of coke, vigorous gas evolution, and pronounced shrinkage during the pyrolysis of phenolic polymers do not permit the full realisation of the potential possibilities of carbonaceous materials obtained from polymers. The inadequate assortment, the limited thickness, the appreciable brittleness, and the presence of undetectable defects in gas-impermeable articles made from carbonaceous materials based on phenolic polymers narrow their practical applications.

The above factors necessitate the search for new polymeric sources of carbonaceous materials which will make it possible to obtain articles with stable and improved characteristics. Polymers with a heterocyclic structure, among which polyimides occupy an outstanding position, can undoubtedly serve as polymers of this kind. The high coke numbers of polyimides, the small gas evolution during their pyrolysis, and the possibility of processing them in a powder form combined with the ability of certain representatives of the polymers of this type to be converted into a highly elastic and viscofluid state justify the assumption that they are promising materials for the creation of thermostable carbonaceous materials with a valuable set of properties.

The present review is devoted to the analysis of studies concerned with modern ideas about processes involving the carbonisation and graphitisation of polymeric materials.† It appeared useful to survey the results of experimental and theoretical studies on processes involving the specific pyrolysis of phenolic polymers, since these have been studied in greatest detail, and polyimides which are some of the most promising representatives of new polymers as potential sources of carbon.

This approach makes it possible to establish important characteristics of the conversion of the polymeric raw material into carbonaceous materials which influence their physicochemical properties.

II. THE FORMATION OF THE STRUCTURES OF CARBONACEOUS MATERIALS ON THE BASIS OF NETWORK POLYMERS

The preparation of carbonaceous products on the basis of polymeric materials involves several heat treatment stages during which their main properties are established.[1,2] In the general case, the stages in the manufacture of carbonaceous materials from polymers are carbonisation and graphitisation. The first stage consists in the heat treatment of the initial raw material (or articles formed from the initial raw material) up to temperatures in the range 1100 to 1300 °C (carbonisation), which makes it possible to obtain under certain conditions carbonaceous materials with a two-dimensionally ordered structure.[1,3] The second stage involves the heat treatment of these materials up to temperatures in the range 2500 – 3000 °C,[1,4] during which mainly their structural rearrangement takes place.

In many instances, additional operations are introduced—preparation of the initial raw material, the moulding of articles, hardening, etc.[1,4] The required form of the article is imparted to the initial polymer which can be cast in the form of a film or moulded in any of the usual ways—by pressing, casting under pressure, and extrusion.[1,5]

It is known[1,6] that the structure and hence also the properties of carbonaceous materials are determined by the nature of the polymer, the character of the intermediate products formed during pyrolysis,

†The review does not present information about processes leading to the formation of carbon fibres, which constitutes an independent field of study.

and the carbonisation and graphitisation conditions. Factors such as the rate of heating to the maximum temperature and maintenance at this temperature can influence significantly the specificity and extent of the thermochemical transformations of the initial raw material and the qualitative characteristics of the materials formed—the crystal and disperse structures, the carbon content, and the concentration of heteroatoms.[1,2]

1. Characteristic Features of the Carbonisation of Phenolic Polymers

The carbonisation of polymeric materials, i.e. their thermal transformation into carbon, is an important stage determining the properties of the final carbonised product. It is achieved by the slow heating of the polymers with and without catalysts in a reducing or inert atmosphere.[7-10] Inert gases (nitrogen,[3,11,12] argon,[13,14] and helium[15]), a high vacuum,[13,16] a coke charge,[17] and a powdered alumina charge[18] were used for this purpose. A reducing atmosphere (H_2, CO) is more rarely employed.[19,20]

The final temperature of the treatment of the polymer is mainly 800–1200 °C,[20,21] although it can be below (600 °C)[11] or above (1400–1600 °C)[12,22] this range. In the carbonisation stage, low-molecular-weight products of the pyrolysis of the polymers are split off, a coke residue is formed, the geometrical dimensions and density of the specimens are altered, and a porous structure and a contact surface are formed. Qualitatively new properties arise in the carbonised polymeric material as a result of these changes.

The onset of the thermochemical transformations of phenol-formaldehyde (FP) and furfural-phenol-formaldehyde (FPF) polymers is believed to be at 150 °C according to electron paramagnetic resonance data.[23-25] When FP and FPF polymers are heated above 300 °C, they begin to undergo degradative changes accompanied by weight loss.[26-29] The principal decrease in the weight of FPF polymers occurs in the temperature range 300–600 °C,[28-30] while the maximum rate of this process has been noted at 460 °C.[1,26] On heating to 1200 °C, the FP and FPF polymers vigorously evolve low-molecular-weight and volatile products[26,27] and the weight loss is then more than 50%.[1,26]

When network polymers are carbonised in the temperature range 250–450 °C, degradative processes, accompanied by the evolution of volatile pyrolysis products and the formation of condensed aromatic fragments, take place preferentially.[25,31] A sharp increase in the concentration of unpaired electrons,[24,30] reaching an extreme value at temperatures of about 600 °C,[23,24] corresponds to this period. Higher temperatures induce the recombination of the aromatic fragments and the appearance of condensed aromatic formations with higher molecular weights.[25,31] The concentration of paramagnetic centres (PMC) then falls sharply.[24]

It has been shown[31,32] that planar layers with hexagonal packing appear in carbonised FP polymers already in the temperature range 200–350 °C.[31,32] However, the hypothesis that the onset of the formation of the structure of carbonised FP and FPF polymers occurs at 500 °C appears more likely.[33] The most intense structural transformations of individual parts of the carbon skeleton of the pyrolysed FP and FPF polymers occur at 500° and 720 °C.[34]

The principal products of the gas evolution in the pyrolysis of the above types of polymers are CO, CO_2, CH_4, H_2, H_2O, and phenol[13,30,34-36] and up to 600 °C mainly carbon oxides and water are evolved, while at higher temperatures the principal products are methane and hydrogen.[36,37]

It has been established[37-39] that, when PF and FPF polymers are heated, they are dehydrated as a result of the interaction between hydroxy-groups, which can take place with cyclisation, and between hydroxy-groups and methylene bridges.

The low apparent activation energy for the dehydration of PF polymers (25–38 kJ mol^{-1}) shows that this process takes place readily.[40]

The maximum rate of evolution of carbon oxides on pyrolysis of FPF and furfural-acetone (FA) polymers is observed at 380° and 500 °C, to which correspond the maxima in the exothermic effect on the differential-thermal analysis (DTA) curves, while the maximum rates of the endothermic evolution of hydrogen and methane have been noted at 390° and 580 °C.[41]

Carbon oxides are formed in the thermal degradation of the least stable oxygen-containing groups at defective sites of the three-dimensional polymer network.[35,42] It has also been reported that CO_2 may be produced as a result of the decomposition of hydroxy- and hydroperoxy-groups formed with participation of chemisorbed atmospheric oxygen[34] and that CO may be formed on decomposition of benzene rings.[26] It has been established[29] that, even at temperatures around 1000 °C, the volatile products of the pyrolysis of PF polymers contain an appreciable amount of CO, while only traces of CO_2 have been noted above 700 °C. The explanation is that at elevated temperatures the reaction equilibrium

$$2CO + O_2 \rightleftarrows 2CO_2$$

is displaced towards the formation of carbon monoxide.

Heating of network polymers above 500 °C leads to far-reaching chemical transformations, which is indicated by the appearance of appreciable amounts of CH_4 and H_2 in the gaseous pyrolysis products.[26,35] Methane is produced as a result of the degradation of methylene bridges, which proceeds via the formation of the reactive methylene radical.[35] This process takes place most vigorously at about 600 °C, above which processes involving the evolution of CH_4 and H_2 predominate. It is emphasised[37,43] that hydrogen may be formed on pyrolysis of PF polymers and also in lower temperature ranges on decomposition of the methylene bridges. At temperatures above 500 °C, the fraction of H_2 increases in the pyrolysis products of the PF and FPF polymers as a result of the dehydrogenation of aliphatic units and the condensation of aromatic rings.[35] It is known[44] that the energy of the C–H bond in the benzene ring is lower than that of the C–C bond, so that on pyrolysis the former is dissociated first. However, Ouchi and Honda[37] have shown that dehydrogenation of aromatic units at high temperatures can be accompanied by the cleavage of the ring with formation of active thermal degradation products and condensed polyphenylene rings.

The dynamics of the specific pyrolysis of PF and FPF polymers is determined by the ratio of the rates of dissociation of the chemical bonds and of the recombination of the radicals formed.

The chemical structure of the polymers undergoes significant changes during heating: the solid coke formed after the removal of the low-molecular-weight products is gradually enriched in carbon and its content of heteroatoms diminishes.[28,32] In the initial stages of the pyrolysis, these transformations are recorded by spectroscopic analysis. Thus the intensity of the absorption bands referring to the OH, CH_2, and C–O–C groups (at 3400, 1475, and 1100 cm^{-1}) gradually decreases in the IR spectra of the heated PF and FPF

polymers.[26,38] This is accompanied by a gradual increase in the concentration of benzene rings, which can be inferred from the increase in the intensity of the 1500 cm^{-1} band.[26,38]

The FPF polymers heat-treated at temperatures up to 500 to 600 °C contain, together with carbon, still a considerable amount of hydrogen and oxygen.[1,31] The 1100 cm^{-1} absorption bands persist in the IR spectra of such materials, while the 1415 cm^{-1} absorption bands, referring to the residual CH_2 groups, completely disappear. Absorption bands charactersitic of condensed aromatic structures appear and grow at the same time.[26,38] The decrease in the concentration of PMC on heating the polymers above 600 °C also indicates vigorous formation of condensed aromatic systems.[1,35] The changes in the polymers can be inferred from their colour. Deepening of the colour to brown and black in the range 300–600 °C indicates the development of a system of aromatised rings.[5] On raising the temperature, further carbonisation of the solid residues in the polymers takes place. For example, heating of the FPF polymers above 1200 °C increases the carbon content in the coke residue from 68.3 to 97.6 wt.% with a corresponding decrease in the oxygen content from 27.1 to 0.3 wt.%.[30] The residual oxygen forms part of the composition of the hexagonal rings and aliphatic units constituting the final network structure of the carbonised material.[1] The hydrogen and nitrogen contents in the carbonised materials diminish,[30] but nitrogen persists in materials heated to 1200 °C (1.8 wt.%).[1]

The study of the processes involved in the heat treatment of resol PF polymers by EPR showed[24] that, up to 500 °C, the density of the three-dimensional polymer (resite) network does not influence significantly the carbonisation process and the structure of the carbonised residue. The greatest changes in the composition of the heat-treated products are observed[24] in the temperature range 500–700 °C, to which corresponds the maximum PMC concentration of $\sim 10^{19}$ to 10^{20} spins g^{-1}. The changes in the paramagnetic properties at temperatures above 500 °C have been attributed[24] to the fact that at this temperature the density of the three-dimensional network of the polymers begins to influence significantly their carbonisation process. The maximum PMC concentration in the region of 600 °C is determined mainly by localised unpaired electrons, which have been identified with ruptured chemical bonds—free radicals.[45–47]

At temperatures in the range 700–750 °C, parallel networks of hexagons begin to be formed in the carbonised materials.[33] It is believed[38] that isotropic regions comprising tiny "crystallites" consisting of non-ordered accumulations of graphite layers are formed at the temperatures indicated. The initial polymer structure disappears fully and the formation of a two-dimensional structure, characterised by a large amount of non-ordered substance, large dimensions of atomic networks, and their imperfect packing is completed.[30,31,33] The transformation of the aromatic molecular chains of the polymer into carbon with a two-dimensional structure takes place within a relatively narrow temperature range, which in fact explains[48] the sharp change in the properties of the materials at 700 °C.

The diamagnetic susceptibility of the carbonised PF and FPF polymers increases above 700 °C, indicating the onset of the growth of hexagonal carbon layers, which continues without interruption as the temperature is raised.[30] The growth of atomic networks, an increase in the size of the crystallites, and an improvement of order are observed in the range 1000–1300 °C.[31,32,49]

The pyrolysis of PF and FPF polymers in an inert atmosphere can be divided into three stages:[42,50,51] 300–350 °C—a slight weight loss and a slight change in volume; 350–(500–600 °C)—vigorous evolution of gaseous pyrolysis products accompanied by weight loss and a decrease in density as a result of the development of an internal porosity; (500–600)–1200 °C—an appreciable intensification of shrinkage with a comparatively small weight loss and an increase in density and thermal conductivity.

The differences between the structures of the initial polymers and in the hardening conditions are responsible for some specificity in their decomposition and influence the yield of the carbon residues.[25,52] It has been shown[53] that, depending on their chemical structure, the FA polymers afford between 53 and 60 wt.% of coke residue. The properties of the carbonised materials are also determined to a large extent by the structure of the initial polymers. Thus the study of the carbonisation of PF polymers established[42] that the density, the overall and open porosities, and the specific electrical resistance of the carbonaceous materials depend on the ratio of formaldehyde and phenol used to synthesise the initial polymers. It has been noted[42] that the PF polymers obtained using a 1.3–1.6 ratio formaldehyde and phenol and heat-treated at 1250 °C give rise to ~70 wt.% of coke residue, show the smallest shrinkage, have the smallest volume of the open porosity, and have the highest density and ultimate bending strength. The carbonisation of polymers obtained using polymer ratios below the limits indicated gives rise to 60–65 wt.% of coke residues, which has been explained[42] by a decrease in the amount of cross-links, formed via bridging methylene groups. Increased formaldehyde content tends to increase the amount of the low-molecular-weight pyrolysis products evolved as a consequence of the decomposition of the excess hydroxymethyl groups, which leads to an increase in the open porosity of the carbonised materials and an impairment of their strength properties.,

A number of workers have emphasised[50,54,55] that the carbonisation stage should be the slowest part of the overall process involving the formation of carbonaceous materials from polymers. The point is that this stage is accompanied by the vigorous evolution of volatile products, generating an internal pressure in the article, which may increase to such an extent that the article ruptures. During the aromatisation of the heat-treated polymeric structures, an impairment of their strength properties is observed with increase in their electrical conductivity.[5] In order to retain strength, it is necessary to suppress the degradation of polymer chains, which is in most cases initiated by free radicals. The procedures for the preparation of carbonised materials are therefore characterised by low rates of temperature rise (1–5 K h^{-1}).[1] The temperature conditions in the carbonisation of porous articles are characterised by higher heating rates compared with the conditions in the preparation of monolithic articles (20–2000 K h^{-1}).[12,22,56]

2. Graphitisation of Carbonised Phenolic Polymers

The graphitisation process is defined as the temperature-activated continuation of the development of the structure of the substance formed in the preceding stages of the heat treatment.[1] This process, whose name cannot be regarded as especially apt when applied to the coke residues from polymers, is accompanied by slight changes in the weight of the specimens, predominantly as a result of the removal of peripheral atoms and groups, further carbonisation, and ordering of the structure.[1–3]

The practical purpose of graphitisation is a sharp reduction of the electrical resistance, the removal of ash impurities, the reduction of reactivity, and the establishment of the required electrophysical properties of the carbonaceous materials.[57]

Polymers whose hardening takes place without the formation of a mesophase serve[2,4] as the raw material for non-graphitisable or hard types of carbon. Such polymers include, for example, the phenolic and epoxide polymers. This fact has been explained[58-61] by the decrease in the mobility of the structural elements of the substance as a result of the formation of bonds in space during the heat treatment. The non-graphitisability of the products of the carbonisation of certain polymers is also attributed to the influence of the extensive pore system, which bends the graphite layers,[48] and the presence in them of nitrogen above 1200–1500 °C, which prevents the condensation and ordering processes.[30]

The studies on the carbonisation and graphitisation processes involving polymers of the vinyl and furan series, PF and FPF polymers, and oligomeric arylenes established[62] that the graphitisability of the carbonised material can be predicted from the activation energy for the main polymer decomposition process in the range 300–500 °C. Thus the activation energies for the polymers investigated are in the range 70–470 kJ mol^{-1}, while the degrees of graphitisation of the carbonised materials vary from 0 to 90%. Processes in which exothermic polycondensation reactions predominate correspond to activation energies below 125 kJ mol^{-1} and the graphitisability of the cokes is then less than 20%. High activation energies (more than 250 kJ mol^{-1}) are characteristic of endothermic degradation reactions of the main chains of the polymer and the degree of graphitisation of such materials is more than 70%.[62]

On heat treatment of carbonised FPF polymers above 1200 °C, a rapid increase of the diamagnetic susceptibility has been noted, which continued without appreciable saturation up to 3000 °C, showing that the structural ordering processes in the test substance have not reached completion.[30]

In carbonaceous material based on PF polymers, the process leading to the perfection of the structure is inhibited, which in fact explains[47] the slow decrease in the paramagnetism of the test specimens heated to 3000 °C. The symmetrical EPR absorption line, observed up to 3000 °C, reflects the imperfection of the structures of such materials, the retention of small size of the crystallites, their enhanced defectiveness, and the absence of a distinct microtexture.[47]

The X-ray diffraction patterns of carbonised PF polymers show reflections of the (001) and (hk0) types, which are approximately at the angular positions corresponding to the graphite lines.[30,31] The high background level persisting on the diffractometer traces for the heat-treated substances is due to the incoherent X-ray scattering by the aromatically non-organised carbon and the different chemical groups consitituting the amorphous phase.[30,31] With increase in the temperature of the heat treatment of the carbonised PF and FPF polymers, their diffraction pattern changes (the reflections become narrower and more intense)—processes leading to the ordering of the material take place, which involves the orientation of the atomic networks, a decrease in the interplanar spacing, the growth of layers of condensed aromatic carbon, a decrease in the thickness of the packets of planar hexagonal layers, and a decrease in the content of the amorphous phase.[30,31] The structural parameters of the carbonised materials vary as follows: the interplanar spacing d_{002} decreases from 0.370–0.360 to 0.344–0.340 nm for the products heat-treated at 900–1200 and 3000 °C respectively. The sizes of the crystallites L_c and L_a then increase from 3–6 and 1.5–2 nm to 6–12.5 and 4.2–4.6 nm respectively.[30,31]

The character of the change in the X-ray diffraction patterns and the structural parameters as a function of the heat treatment temperature shows that the carbonised PF and FPF polymers are typical non-graphitisable materials with a turbostratic structure.[30] They are characterised by small dimensions of crystallites, are isotropic, have an extensive microporosity and transitional porosity, and their crystal structure remains of the turbostratic type up to high temperatures—as far as 2800–3000 °C.[1,2]

It has been shown[6] that, despite the appreciable changes occurring in the structure of carbonaceous materials based on phenolic polymers during heat treatment, the qualitative character of the globular-cellular structure of the initial polymer is retained up to 3000 °C. The degeneration of the globules to highly oriented regions and the subsequent formation of graphite on the latter proceed with a lag period because this structural rearrangement involves translational processes. It has also been established[6] that the process leading to the imperfection of the structure of the carbonaceous materials based on PF polymers is accompanied by a change in the shape of the globules from spherical to ellipsoidal.

The study of a series of carbonised phenolic polymers—derivatives of phenol, *m*-cresol, and 3,5-xylenol heat-treated at 3000 °C—established[63] that the graphitisability is determined by the structure of the phenolic fragment. The presence of the bulky CH_3 substituents in the phenol improves the graphitisability of the carbonised polymers. Thus non-graphitisable "hard" carbon is obtained from PF polymers, graphitisable or "soft" carbon is obtained from xylenol-formaldehyde polymers, while cresol-formaldehyde polymers give rise to a carbon of an intermediate type.[63] The three-dimensional (112) diffraction line, indicating the appearance of the graphite phase in the test substance, has been noted for carbonised xylenol-formaldehyde polymers at 1800 °C, while for the other two polymers it remained weak even at 3000 °C.[64]

It was established later[65] that mesophase mosaic formations arise in the heat-treated xylenol-formaldehyde polymers at 400–430 °C and promote the formation of large condensed aromatic structures in the test substance, which leads to effective graphitisability of carbonised polymers of this type.

It has been shown[64] that the (002) reflections for carbonaceous materials derived from PF polymers at temperatures above 2800 °C and for materials obtained from cresol-formaldehyde polymers at 2950 °C are compound, while in the case of xylenol-formaldehyde polymers single reflections are obtained. This indicates the presence in the first two specimens of regions differing greatly in the type of structural organisation.

The character of the changes in the compound (002) profile with increase in temperature made it possible to represent the graphitisation process in the following way.[63,64] The distance d_{002} in the initial crystallite of the non-graphitisable carbonaceous material gradually diminishes with increase in the heat-treatment temperature. When d_{002} and L_c reach 0.343–0.344 nm and 2–4 nm respectively, a small proportion of the heat-treated substance changes abruptly. Three components having different structural parameters then appear in the material (see Table).

A further increase in temperature leads to an increase in the amount of the graphite component where d_{002} = 0.336 nm, but even at 3000 °C all three components coexist.[64] It is noteworthy that L_c in the graphitisable carbonaceous material depends on the interplanar spacing, while in the non-graphitisable material it does not. Furthermore, the structural parameters of the graphitisable carbonaceous material vary monotonically and those of the non-graphitisable carbonaceous material vary step-wise.[64]

The study of the processes leading to the formation of the porous structure of the FPF polymers during their heat treatment up to 3000 °C has shown[56] that the pores in such materials can be represented by a honeycomb with a cell size of 10–30 nm and a wall

thickness of 5 – 15 nm. The walls of the pores have in their turn much smaller pores.[66]

As the temperature of the heat treatment is reduced, the macroporosity of the carbonaceous materials based on PF and FPF polymers greatly diminishes (from 13% at 1000 °C to 2.3% at 3000 °C).[6] The size of the intraglobular pores and the structural porosity increase under these conditions. The abrupt change in the structural parameters and the character of the distribution of the porosity during the heat treatment of carbonaceous materials suggested[6] that the decrease in porosity takes place not only as a result of the condensation and ordering of the carbonaceous material but also as a result of the generation of crystalline closer-packed graphite-like formations.

Structural parameters of the carbonaceous materials based on phenolic polymers.[64]

Initial polymer	T, °C	d_{002}, nm	L_c, nm
PF polymer	2800	0.3437	2.3
	2800	0.3427	84.0
	2800	0.3863	66.0
	3000	0.3430	3.3
	3000	0.3427	28.0
	3000	0.3370	37.0
Cresol-formaldehyde polymer	2950	0.3448	2.7
	2950	0.3430	8.0
	2950	0.3373	37.0

The graphitisability of carbonised polymers is known to depend on several factors: the rheological properties of the initial polymers, the nitrogen content in the carbonised residues, and the number and energy of the transverse spatial bonds in them[1,48,59] It has been established[67] that the graphitisability of the carbonised materials can be regulated by pressure. However, there is no information in the literature about the influence of each of the above factors on the graphitisability and structure of carbonaceous materials based on polymers.

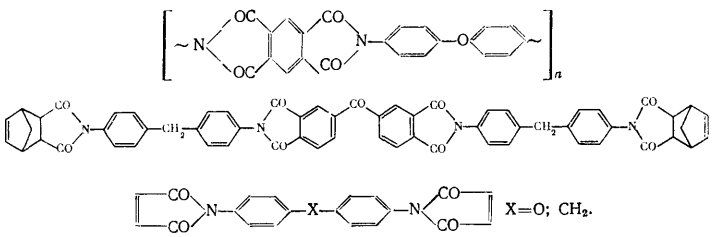
III. SPECIFIC PYROLYSIS OF POLYIMIDES

Numerous communications devoted to the thermal degradation processes involving aromatic polyimides have now been published.[68–87] Depending on their chemical structure, polyimides are distinguished by a wide variety of properties and there are numerous literature data concerning the influence of their structure on their thermal stability.[70–75] Data concerning the influence of the chemical structure of polyimides on their thermal stability in an inert atmosphere have been surveyed in a monograph.[88] It is believed[85] that the degradation of polyimides begins as a result of the decomposition of the "binding" elements—the imide ring and the bridge structures (atoms and groups of atoms).

The chemical structure of polyimides influences significantly the pathways followed in their thermal decomposition.[68,78,85] The polyimide thermal degradation processes can be determined to a large extent by the presence in them of heterounit fragments: amidoacid and isoimide structures and terminal functional groups.[88,89]

The pyrolysis of polyimides is known[85] to proceed via a series of consecutive-parallel reactions, each of which is associated with the formation of definite products. This process is accompanied by the formation of gaseous, liquid, and solid low-molecular-weight substances and of an infusible high-molecular-weight residue. The main bulk of the low-molecular-weight polyimide degradation products consist of H_2O, CO, CO_2, H_2, phenol, benzene, analine, and benzonitrile.[78,79,82,90] The solid polyimide pyrolysis products consist of aromatic carbocyclic and heterocyclic compounds with a system of conjugated double bonds. At the same time, the processes involved in the specific pyrolysis of polyimides, whose aim is to obtain carbonaceous materials, have been investigated to a much smaller extent.[90–94]

The transformations of polyimide and oligoimides having the following structure have been investigated[90] on heating to 3000 °C:



X=O; CH_2.

Carbonaceous materials have been obtained from the polymers and some of their properties have been investigated (hardness, specific surface, and tensile strength). A general scheme for the pyrolysis of polyimides has been published[69] with references to known sources (Fig.1).

In our view, the data on the temperature ranges corresponding to the formation of certain low-molecular-weight pyrolysis products obtained as a result of X-ray diffraction studies and their interpretation are controversial.

The studies on the transformations at temperatures up to 3000 °C in non-oxidising media (argon, coke charge) of polyimides obtained from pyromellitic acid and *p*-phenylenediamine (I), from pyromellitic acid and di(4-aminophenyl) ether (II), from benzophenone-3,3′,4,4′-tetracarboxylic acid and di(4-aminophenyl) ether (III), and from benzophenone-3,3′,4,4′-tetracarboxylic acid and anilinofluorene (IV) have shown[95–97] that the changes in the structure and properties of the polyimides on heating take place at temperatures in the range 300 – 500 °C in a relatively stable mass. Under these conditions, the glass points of the polyimides (III) and (IV) increase gradually and the polyimide (IV) loses it solubility, which may indicate the formation of intermediate three-dimensional structures.

Polyimides may be cross-linked as a result of the interaction of the terminal amino-groups with the imide ring,[83] the interaction of the amide and terminal amino-groups,[88] and the dehydrogenation coupling of two phenyl groups.[85]

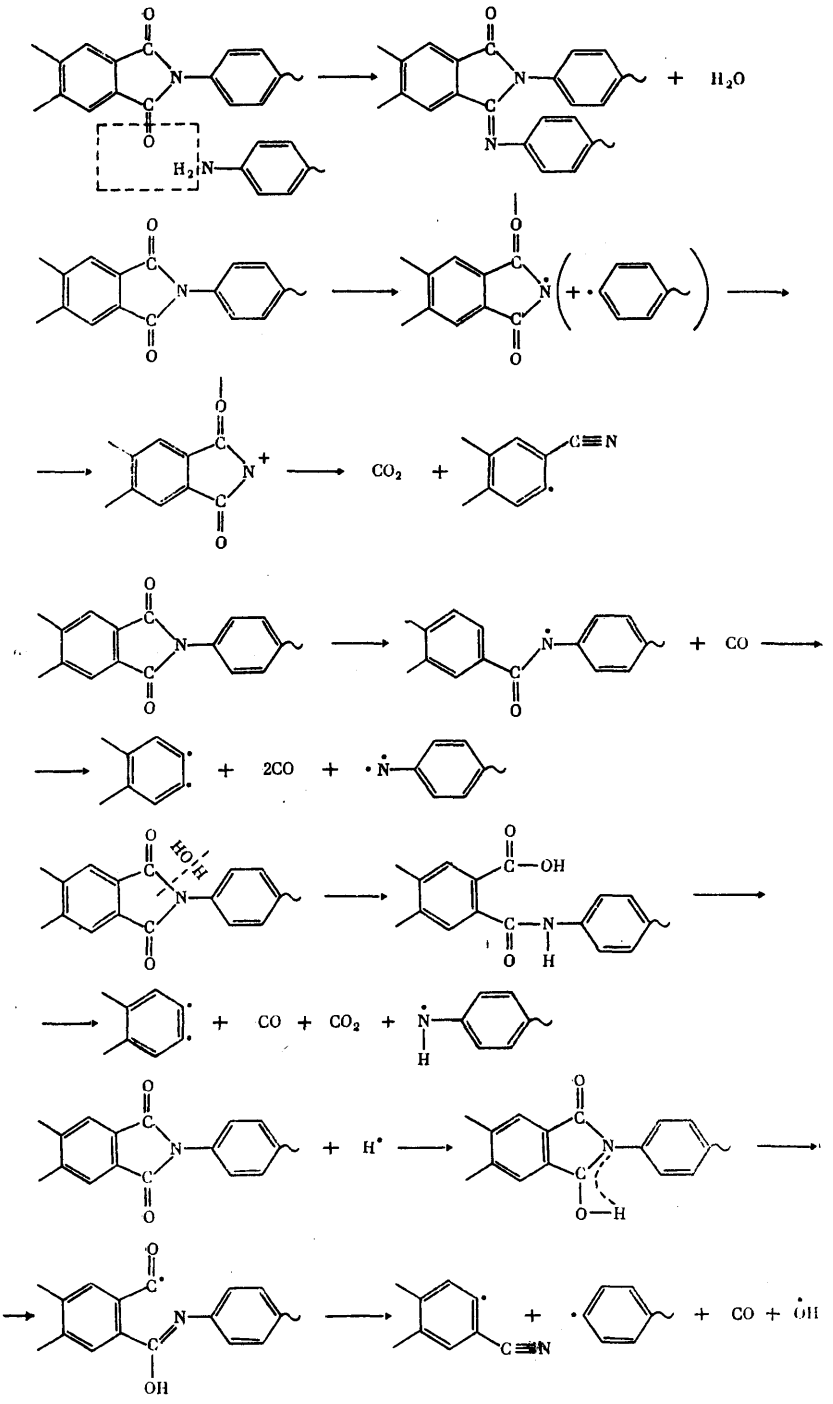
Absorption bands at 1650 cm^{-1} (amide), which can be partly attributed to the formation of a three-dimensional network in polyimides, appear in the IR spectra of heat-treated polyimides.[95,97] The fragments formed under these conditions can serve as sources of certain low-molecular-weight pyrolysis products and can influence the course of the subsequent transformations.

The heating of polyimides in argon to 520 – 540 °C and of the polyimide (I) to 580 °C reduces their weight as a result of the removal of low-molecular-weight pyrolysis products, which consist of carbon oxides and water. The formation of the above products in the initial stages of the weight loss process can occur as a result of a series of elementary reactions[98] (see below).

Under real conditions, the pattern in the thermal degradation of polyimides is much more complex even in the initial stages of the weight loss. It is known[85] that, under the conditions of dynamic heating, there is a possibility, in principle, of any bond dissociation reaction with formation of the corresponding products.

A decrease in the intensity of the 1780 (in a doublet with 1720), 1380, and 725 cm^{-1} absorption bands and an increase in the intensity of the 1650 cm^{-1} band have been observed in the IR spectra of the polyimides (II)–(IV) heat-treated at 540–550 °C.[95-97] These changes indicate the continuation of the reactions in the polyimides.

Heat treatment of the polyimides (II)–(IV) above 550 °C and of the polyimide (I) above 630 °C leads to the development of their thermal degradation processes, which are determined by competing reactions involving the rupture of the spatial cross-links and intramolecular bonds and polycondensation. Under these conditions, the rates of weight loss by the polyimides increase sharply, the



amount of low-molecular-weight pyrolysis products increases, and their composition changes (Fig.2). According to EPR data, the most intense degradative changes, accompanied by the dissociation of chemical bonds and the formation of free radicals, occur in the temperature range 550–650 °C. For the polyimide (I), these processes have been displaced by about 50 °C to the high-temperature region. Most of the weight loss by polyimides occurs in these ranges.[95-97] The degradation of polypyromellitimides, associated with large weight losses, takes place in the narrowest temperature ranges, compared with the polyimides formed from diphenyl ether derivatives and benzophenonetetracarboxylic acid.[95-97]

The rates of decrease in the weight of the polyimides (I) and (III) in the intense degradation region are higher by a factor of 3–4 than those of the polyimides (III) and (IV).

The effective activation energies for the intense polyimide degradation processes in the region of the main weight losses are E_{eff} = 170–300 kJ mol^{-1},[95] E_{eff} for polypyromellitimides being higher by a factor of ~1.5 than E_{eff} for polyimides formed from diphenyl ether derivatives and benzophenonetetracarboxylic acid.

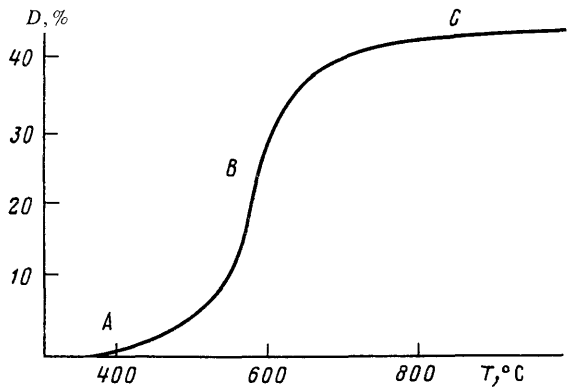
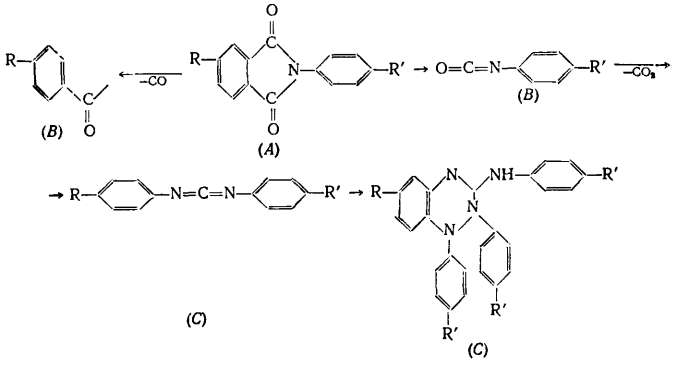


Figure 1. Schematic representation of the pyrolysis of polyimides:[90]



The letters *A*, *B*, and *C* denote regions corresponding to the existence and transformations of the corresponding structures; *D* = weight loss.

Indeed the low activation energy for thermal degradation means that, with increase in temperature, the thermal degradation of polyimides is not accelerated quite so much as that of the polymers with a high activation energy and the advantage of the former will become most apparent at high temperatures. With increase in the mobility of the polyimide macromolecules, the contribution of condensation processes in pyrolysis increases, which may be the cause of the reduced effective activation energies for the thermal degradation processes involving such polymers. Indeed, an increase in chain mobility creates favourable kinetic conditions for the recombination of the fragments produced.

The main bulk of the low-molecular-weight products, whose qualitative composition varies significantly compared with the initial pyrolysis stages, are removed from the polyimides (III) and (IV) at temperatures in the range 550–650 °C. Thus, apart from carbon oxides and water, whose formation was noted already at temperatures corresponding to insignificant weight losses and whose amount increases with increase in temperature, hydrogen, nitrogen, hydrogen cyanide, methane, benzene, phenol, benzonitrile, and diphenyl ether have been identified in the polyimide pyrolysis products (Fig.2). The formation of the above products from the polyimide (I) takes place at higher temperatures (600–700 °C).

The overall amounts of the low-molecular-weight products as well as their composition are comparable for the polymers investigated. Nevertheless, the influence of the chemical composition of the polymers on the character of their thermal degradation can be traced quite distinctly.

The main fraction of the polyimide pyrolysis side products, evolved in the region of vigorous degradation, corresponds to CO and CO_2 (Fig.2); H_2O is also formed in considerable amounts. The maxima of the peaks in the mass spectra of the above products correspond approximately to the temperatures of the highest rates of weight loss.[95-97]

It is noteworthy that the polyimides (I) and (II) evolve larger amounts of CO_2 than CO, while the polyimides (III) and (IV) exhibit the opposite behaviour. The CO_2/CO ratio for the polyimide (I) is greater than for the polyimide (II), which may be due to the high extent of the intramolecular and intermolecular interaction of the donor (diamine) and acceptor (dianhydride) sections in the polyimide macromolecules. It is known[99,100] that such interaction is accompanied by the delocalisation of electrons and the formation of intramolecular and intermolecular charge-transfer complexes. The possibility of an intramolecular rearrangement or of intramolecular oxygen transfer is facilitated in formations of this kind, which promotes the reaction involving the decomposition of the imide ring with formation of CO_2. The bridging heteroatoms or groups of atoms interrupt or greatly weaken the conjugation along the chain.[100] The electron-donating properties of the diamine residues weaken from the polyimide (I) to the polyimide (II), which can explain the changes in the ratio of the carbon monoxide and dioxide formed.

The higher CO content in the pyrolysis products of the benzophenonetetracarboxylic acid polyimides may be caused by the splitting-off of the carbonyl groups from the benzophenone structure.[101] The somewhat smaller, compared with the polyimide (III), amounts of CO formed in the pyrolysis of the polyimide (IV) are probably associated with the influence of the carbo-group.

The intensity maxima on the curves describing the formation of the low-molecular-weight liquid products of the pyrolysis of polyimides correspond to the region of high rates of weight loss (Fig.2). The greatest relative amounts of liquid compounds are formed in the thermal degradation of the polyimides (I) and (II).[95-97]

The formation of the products described indicates a far-reaching rearrangement of the chemical structures of the polyimides on heating. The evolution of such compounds by the polyimides under the

conditions of specific pyrolysis should probably be explained, by analogy with the pyrolysis of the network polymers (PF and FPF), by the removal of bulky fragments preventing the molecular condensation of the heat-treated polyimides. Such fragments may be structural elements arising in the initial stages of the pyrolysis and also sections of the macromolecules which were not altered at lower temperatures.

In the heating process, the elemental composition of the coke residues from the polyimides changes, which is particularly notable at the temperatures corresponding to the removal of liquid low-molecular-weight pyrolysis products. At 600–700 °C, the carbon content in the residues increases to 80–86 wt.%, while the fraction of hydrogen and nitrogen diminishes appreciably.[95-97]

Pyrolysis of the polyimides leads to the formation of new products—carbonised polyimides—at temperatures in the range 600 to 700 °C.

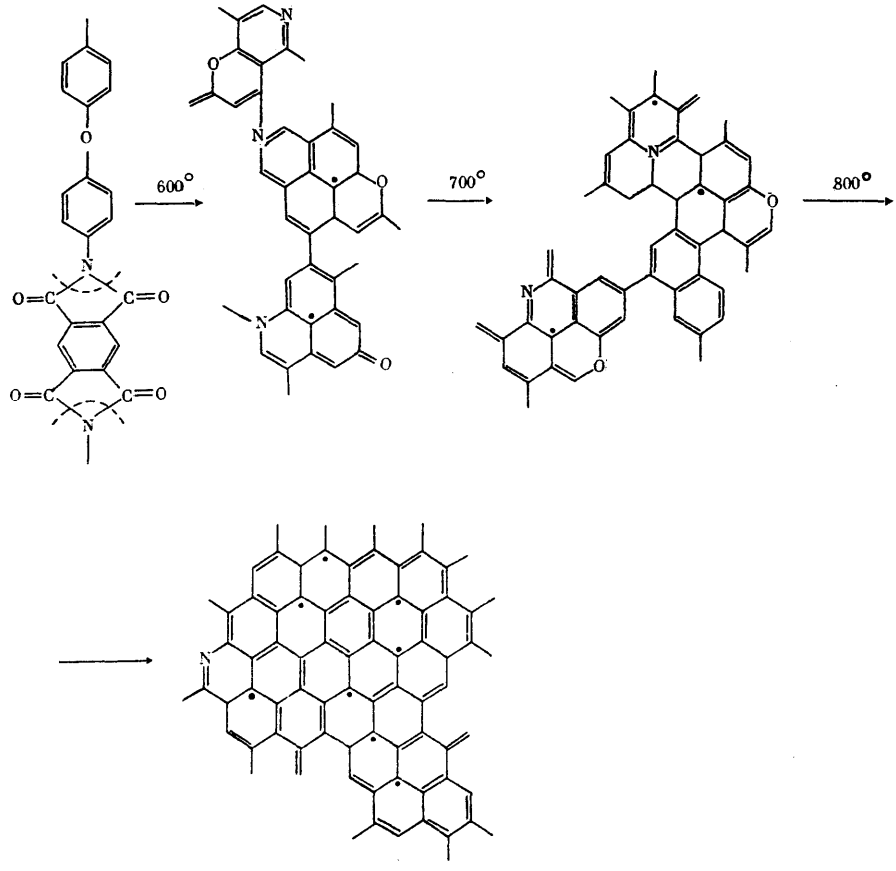
X-Ray diffraction data indicate the conversion of the chain structure of the polyimides to a polycyclic condensed structure at temperatures in the range 600–700 °C. The properties‡ of the pyrolysed materials change sharply at these temperatures—they acquire metallic lustre, their electrical resistance decreases to 180–210 Ω cm, and their thermal expansion coefficients and thermal diffusivities increase respectively from 0.2–0.3 (for the unheated polyimides) to 0.5–2.0 $W\ m^{-1}\ K^{-1}$ and from (1.1–1.3) × 10^{-7} to ~4.0 × 10^{-7} $m\ s^{-1}$.[95-97]

It has been shown[102] that the bulk-phase electrical resistance of the Kapton polyimide film decrease by 16–18 orders of magnitude after vacuum heat treatment at 600–800 °C as a result of the formation of carbon–carbon double bonds and free valences in the polymer.

The yield of coke from the polyimides (I)–(IV) at 900 °C in argon is 55–64 wt.%. The greatest amounts of residues are retained by polyimides with bridging atoms in the dianhydride residues.[95-97]

It has been shown[87] that, in polymers having a heterocyclic structure, nitrogen participates in the formation of the coke residue together with carbon. The nitrogen of the phthalimide ring, a considerable proportion of which is retained in the carbonised polyimide at 1000 °C, plays the greatest role in this process.[87]

The study of the vacuum thermal degradation of polyimides with an increased nitrogen content and based on the di- and tri-phenyl derivatives of pyridine and diamines containing pyridine, benzimidazole, and oxadiazole rings has shown[87] that the coke residues from such polymers amount to 60–65 wt.% and that their content is



‡The properties are quoted for specimens in bulk.

independent of the initial structure of the polyimides. The carbonised materials retain on average up to 50–60% of nitrogen relative to its initial amount. It has also been established[87] that, compared with the thermal degradation of polyimides containing nitrogen atoms only in the imide rings, the relative nitrogen content in the coke residue from polyimides with an enhanced [initial] nitrogen content is reduced by 10–15%. It has been suggested that the nitrogen atoms not forming part of the imide ring participate in the formation of volatile thermal degradation products, while the imide ring nitrogen is mainly concentrated in the coke residue.[87] However, the observed characteristics of the pyrolysis of polyimides having different chemical structures[95–97] [(I)–(IV)] suggest that the character of the elimination of nitrogen when they are heated is determined to a large extent by the rheological properties of the initial polymers.

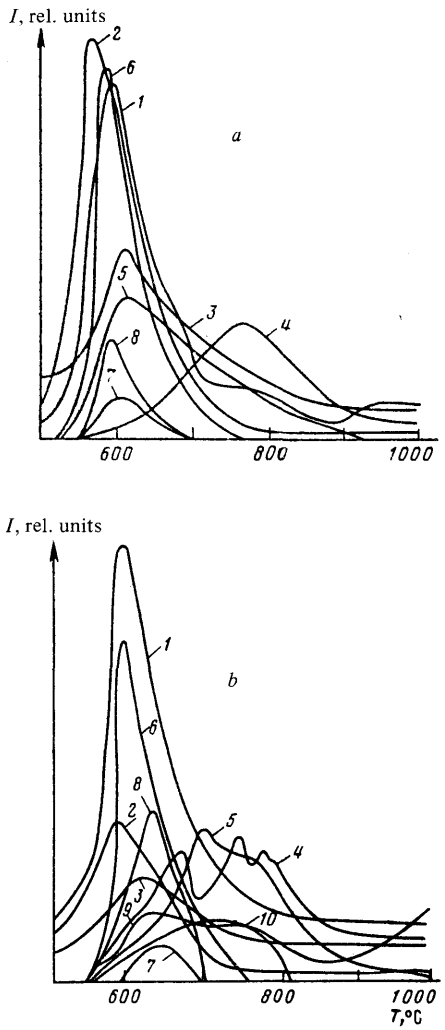


Figure 2. Differential curves for gas evolution in the pyrolysis of polyimides (II) (*a*) and (IV) and (*b*): (1) CO; (2) CO_2; (3) H_2O; (4) H_2; (5) HCN; (6) phenol; (7) benzene; (8) benzonitrile; (9) N_2; (10) CH_4.[96]

Fig.2 shows that the main fraction of the nitrogen-containing pyrolysis products in the thermal degradation of polypyromellitimides is removed before this is observed for polyimides derived from diphenyl ether and benzophenonetetracarboxylic acid.

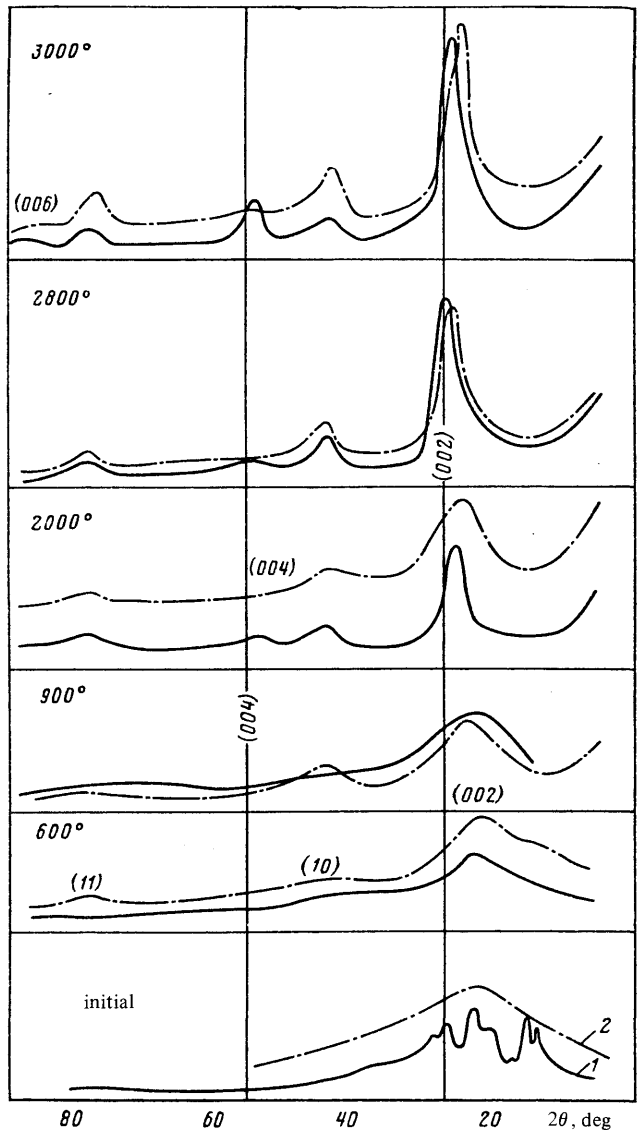


Figure 3. X-Ray diffractometer traces for the initial polyimides (II) (curves *1*) and (IV) (curves *2*) and the carbonaceous materials based on them; heating rate 5–20 K h^{-1}; the vertical lines indicate the angular positions of the principal graphite reflections.[96]

The above factors suggest that the pyrolysis of polyimides with different structures leads to the formation of carbonised materials having different structures. This is manifested particularly strongly when two groups of polymers are considered: polyimides without bridging atoms or groups of atoms in the dianhydride fragments

(polypyromellitimides) and polyimides with the benzene rings in the dianhydride and diamine components separated by such groups—polyimides derived from diphenyl ether and benzophenonetetracarboxylic acid.[95-97] Thus, when the carbonised polyimides (I) and (II) are heated, nitrogen-containing compounds are eliminated initially, which should evidently promote the condensation of these substances, and this is followed by further aromatisation accompanied by the removal of hydrogen, while in the case of the carbonised polyimides (III) and (IV) these processes take place simultaneously.

Heat treatment of the carbonised polyimides in the temperature range 900–3000 °C is accompanied by slight (from 3 to 7%) weight losses and the rates of shrinking processes diminish, approaching zero at 2000 °C. The overall shrinkage is then 16–18%.[95-97] Heat treatment of the materials above 2000 °C leads to the virtually complete elimination of hydrogen from them, the carbon content in the specimens heated to 2500–3000 °C being 99.3–99.9%. It must be emphasised that nitrogen was not detected in the carbonaceous materials based on the polyimides of the first group, obtained at temperatures in the range 1500–1800 °C, while the materials based on the polyimides of the second group retain considerable amounts of nitrogen (0.20–0.33 wt.%) after heating to 3000 °C.[95-97]

During the high-temperature treatment of the carbonised polyimides, the X-ray diffraction patterns change (Fig.3). With increase in the heat-treatment temperature, the intensities of the diffraction profiles of the polyimides increase and the (002) line shifts to the region of larger angles. The improvement of the structure of the carbonised substances is also indicated by the appearance of the (004) line on their diffractometer traces.

The narrowing of the diffraction peaks and the increase in their intensity with increase in the heat treatment temperature and the appearance of the (004) line on the X-ray diffraction patterns indicate the continuing ordering of the structures of the carbonaceous materials.

The form of the X-ray diffraction patterns and the character of the changes in the structural parameters of the carbonised polyimides demonstrate that they are typical non-graphitisable materials with a turbostratic structure.

Materials obtained from polypyromellitimides have the most perfect structure. Their X-ray diffraction patterns show the most intense reflections; after heat treatment at 2950 °C, the (006) lines appear, indicating "long-range order" in the substance (Fig.3). The interplanar spacing in the crystals of the carbonaceous materials obtained from the polyimides (I) and (II) is 0.338 nm, whereas for the remaining materials it is 0.343–0.344 nm. The fraction of the amorphous phase in materials obtained by the heat treatment of polypyromellitimides at 2800 °C is 42% compared with 48–53% for the materials based on the polyimides (III) and (IV).[95-97]

The change in the structural parameters of the crystallites of the carbonaceous materials based on polyimides (Fig.4) is associated with the changes in their chemical composition. The fastest decrease in the interplanar spacing is observed at temperatures such that the processes involving enrichment in carbon and the elimination of nitrogen proceed at high rates; this happens in the range 600 to 1200 °C for the polyimides (I) and (II) and 600–1500 °C for the polyimides (III) and (IV). Above the temperature ranges indicated, the rate of decrease in the interplanar spacing diminishes and the rate of increase in the crystallite diameter appreciably increases. For carbonised materials obtained from the polyimide (IV), this process is particularly vigorous, as a result of which their crystallites have the highest diameter among the materials investigated. Presumably this is associated with the presence in the polyimide (IV) macromolecules of fluorene groups, which, as a result of the thermal transformations in the temperature range 1200–1500 °C, acquire the ability to be located in the planes of different sections of the main chain, having the most ordered structure. The decrease in the diameter of the crystallites in materials based on the polyimide (II) (Fig.4) is due to vigorous processes involving the mutual approach of the hexagonal layers, which may induce their rupture at the most strained bonds.

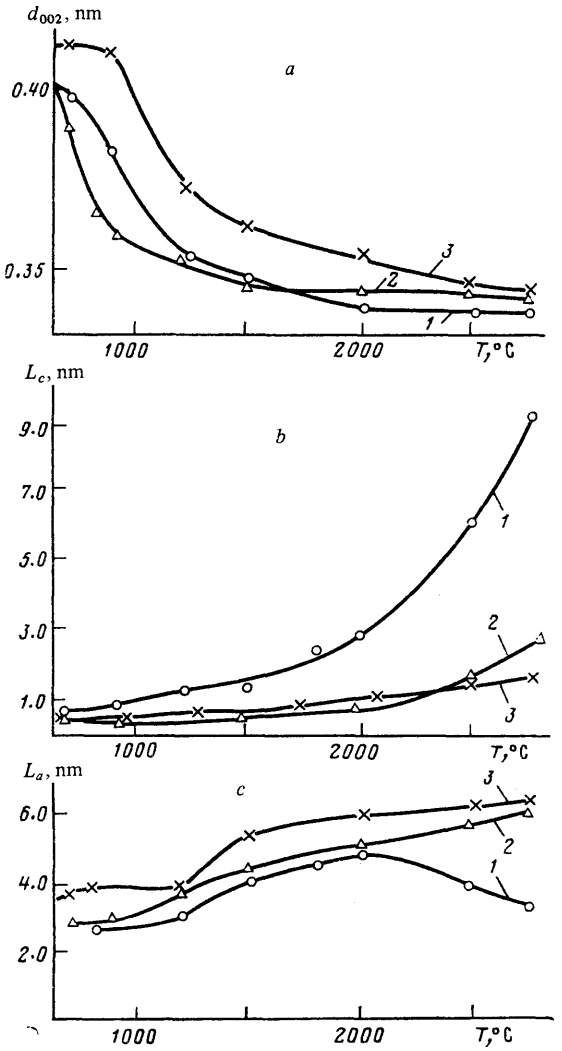


Figure 4. Variation of the interplanar spacing (d_{002}) (*a*), of the thickness of the packets (L_c) (*b*), and of the layer diameter (L_a) (*c*) in the carbonaceous materials based on the polyimides (II) (curves *1*), (III) (curves *2*), and (IV) (curves *3*) as a function of the heat treatment temperature; heating rate 5–20 K h^{-1}.

An increase in the thickness of the crystallites is observed mainly at temperatures where the materials contain the minimum amounts of nitrogen possible for them (Fig.4). Indeed, the growth in thickness of the crystallites in the specimens based on the polyimide (II) is

observed already above 600 °C. The high rates of growth of the height of their crystallites are probably associated with the absence of nitrogen from such materials, heated above 1500 °C.

The data presented show that the structural differences between the carbonaceous materials based on polyimides are mainly associated with the nature of the removal of nitrogen from them. This nitrogen, which has a relatively larger molecular volume than carbon, can prevent the ordering of the structure of the carbonaceous substances.[1,47,103]

It must be emphasised that significant differences between the characteristics of the removal of nitrogen from the polyimides investigated were noted already in the early stages of pyrolysis.

The foregoing suggests that the spatial cross-links, formed in the polyimides in the early stages of the thermal degradation, arise mainly with participation of the nitrogen of the imide ring and prevent its elimination. In carbonaceous materials with a relatively low degree of order [based on the polyimides (III) and (IV)], a considerable nitrogen content has been observed even at 3000 °C, while in the materials based on the polyimides (I) and (II) nitrogen was no longer detected above 1500 °C. One must evidently assume that the spatial cross-linking of polypyromellitimides also takes place, but in such cases it occurs at energetically unfavourable sites. Consequently spatial bonds with different thermal stabilities may arise in the heat-treated polyimides. The weakest of them are ruptured, providing the main source of nitrogen removed from the carbonised materials above 1000 °C, while the strongest are retained up to 3000 °C.

It has been shown[95-97] that the degree of ordering of the structures of the carbonised polyimides is largely determined by the stability of the intra- and inter-molecular cross-links formed in them on heating with participation of the nitrogen of the imide ring. The frequency of such cross-links is known[104] to be capable of varying significantly under the influence of mechanothermal influences, which leads to definite possibilities for regulating the structures of the carbonaceous polyimide-based materials.

The characteristics of the changes in the structural parameters of such materials are determined by the differences between not only their chemical structures but also between their supermolecular structures. Indeed, transient forms of carbon are formed as a result of the reactions in the solid phase, which leads to the possibility of the retention of the initial form of the materials.[4,105]

It has been suggested that the conformation of the skeleton of the polyimide (I) chains can be represented as a planar zig-zag,[106] while for the polyimides (III) and (IV) it can be represented by a greatly extended helix.[88] Sections with different degrees of order can exist in such structures.[107]

The size of the crystallites in the carbonised polyimides is much smaller than that of the crystallites in the carbonised PF and FPF polymers,[30,31] which leads to the expectation that the carbonised polyimides have enhanced strength properties. The wide set of interplanar spacings of the carbonaceous materials obtained from polyimides having different chemical structures provides different possibilities for regulating their physicomechanical characteristics.

The carbonaceous materials obtained from polymers consist of a broad spectrum of molecular structures and supermolecular formations: chain, layer-ribbon, globular, lamellar, diamond-like, and graphite-like formations.[108] The wide variety of structural forms of the artificial carbonaceous materials presuppose a correspondingly wide range of their possible properties.[58,108] By regulating the structure of the material by means of heat treatment or by selecting the initial raw material, it is possible to regulate its characteristics.

Thus vitreous carbon, having many specific properties which are not characteristic of the known modifications of carbon, has been obtained from many types of polymers.[109-117] These properties include an isotropic and monolithic structure, low permeability to liquids and gases, effective strength characteristics, high electrical and thermal conductivities, high thermal stability (in non-oxidising media as a function of the final synthesis temperature—1200 to 3000 °C), high resistance to thermal shock, low density, and resistance to corrosive media which is retained at elevated temperatures.[112-116] Vitreous carbon remains solid up to the sublimation temperature of carbon (3700 °C).[1]

The increase in the chemo-oxidative and thermo-oxidative stabilities and the virtually complete absence of open porosity in vitreous carbon permits its use under conditions where graphite articles break down—in corrosive media and at elevated temperatures and also at an interface between two media. Vitreous carbon articles are used as heat exchangers, components of nuclear reactors and flying vehicles, electrical conductors, electrodes and electric terminals; crucibles, bulb containers, and chemical apparatus for use in specially corrosive media, and implanted components are made from it.[111-117]

The characteristics of the structure and the properties of vitreous carbon have been investigated in detail.[118-122]

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The Influence of the Surface on Phase Transitions in Two-component Systems

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The results of theoretical and experimental studies on phase transitions in semi-infinite two-component systems (immiscible liquids and polymer systems) are examined. The conditions for the formation on the substrate surface of a wetting layer of one of the equilibrium phases are discussed in detail within the framework of the average field theory taking into account the small-radius interactions between the substrate and the mixture components. The theoretical conclusions are compared with experimental data. The role of the long-range forces in the wetting transitions and the appearance of anomalously large fluctuations in the wetting films are considered in relation to the simplest models. The results of the study of critical adsorption are briefly described.
The bibliography includes 156 references.

CONTENTS

I.	Introduction	1013
II.	Phenomenological theory of phase transitions in semi-infinite systems	1013
III.	Cahn's theory and experimental studies on wetting transitions	1015
IV.	Generalised phase diagrams and surface spinodal curves	1018
V.	Phase transitions in semi-infinite polymer systems	1020
VI.	The role of long-range forces in wetting transitions	1022
VII.	Fluctuations in the wetting layers and critical parameters of wetting transitions	1023
VIII.	Critical adsorption	1024

I. INTRODUCTION

The idea, formulated in the 1960's, that fluctuations play a decisive role in the universal behaviour of various systems near the critical point (CP) has been the basis of modern theories of critical phenomena. The scaling theory and the renormalised group method[1-3] have provided a new stimulus to the study of phase transitions (PT).[4-6] Systems whose components are high-molecular compounds (solutions and mixtures of polymers) were added to the traditional objects of study (magnetic substances, alloys, liquids, two-component liquids, etc.).[7-11] The improvement of the experimental technique and the development of novel methods have made it possible to find more accurately the critical parameters characterising the variation of properties in the vicinity of the CP and to conclude that polymer systems belong to the same class, in terms of their universality, as liquids and binary mixtures of liquids.

Together with the continuation of studies on PT in the bulk phase,[12,13] the study of PT in bounded systems is of great interest. Initially the question of the influence of the surface of the substrate on the PT was considered within the framework of Landau's theory[14] applied to the magnetisation of ferromagnetic substances[15,16] and the superfluidity of helium.[17] The transition from limited to complete wettability of the surface near the CP for two-component and pure liquids has been analysed.[18,19] The characteristic features

of the PT in semi-infinite systems discovered in the above studies have attracted the attention of many investigators to this problem and at the present time various questions concerning wetting transitions are being actively elucidated.[20,21] This field of knowledge is going through a period of rapid development, associated with the appearance of an increasing number of new facts. The present review is devoted to the analysis of the behaviour of liquids with limited miscibility and polymer systems in the vicinity of the surface of the substrate. The questions discussed here, concerning the conditions governing the appearance of a wetting layer of one of the equilibrium phases, the order of the transition from complete wetting to limited wetting, and the phenomenon of critical adsorption, are analysed within the framework of the average field (AF) theory.

II. PHENOMENOLOGICAL THEORY OF PHASE TRANSITIONS IN SEMI-INFINITE SYSTEMS

The modifying effect of the substate on PT has been analysed in detail within the framework of the phenomenological theory, whose universal procedures make it possible to consider different phenomena such as surface magnetisation.[15,16,20,22] the superfluidity of helium near the λ-point,[17] and wetting transitions in immiscible liquids.[23]

The fundamental postulates of the phenomenological theory reduce to the following: (1) by analogy with the theory of PT of the second kind,[14,17] it is assumed that in the vicinity of the transition point the free energy density $f(\psi)$ can be expanded in series in terms of the order parameter ψ:

$$f(\psi) = C\psi^2 + D\psi^4 - h\psi, \tag{1}$$

where $C = C_0 t$ and C_0 and D are positive constants. Here and henceforth $t = (T - T_c)/T_c$, T is the temperature, and T_c is the critical temperature. For a two-component system, the deviation of the concentration φ from the critical value φ_c is chosen as ψ, whereupon h characterises the deviation of the difference between the chemical potentials of the components $\Delta\mu$ from the corresponding difference on the coexistence curve $\Delta\mu_c$; $h = (\Delta\mu - \Delta\mu_c)/k_B T$. (2) The wall infringes the spatial invariance of the system and in the boundary layer of the specimen the order parameter is different from its bulk-phase value. The increase in the free energy of the system as a result of the spatial inhomogeneity which has arisen at the boundary is taken into account by introducing a term proportional to the square of the gradient of the order parameter. (3) It is assumed that the forces acting from the sides of the substrate on the system involve only the first layer of molecules, which makes it possible to take into account the contribution to the free energy of the system by the interactions of the substrate with the molecules in the nearest layer with the aid of the term F_s.

Then, neglecting fluctuations and assuming that $\psi(z)$ is the average value of the order parameter in a plane parallel to the surface of the substrate and separated from it by a distance z, the free energy functional of the semi-infinite system can be written in the following form:[20]

$$F[\psi] = F_s + \int_0^\infty dz \left[f(\psi) + \frac{1}{2} k (\nabla\psi)^2 \right], \tag{2}$$

where $k > 0$ is assumed to be constant. The difference between the properties in the surface layer and in the bulk phase promotes the formation of the order parameter profile ensuring a minimum in the free energy of the system. The spatial distribution of $\psi(z)$ is obtained by solving Euler's equation:

$$k \frac{d^2\psi}{dz^2} = \frac{\partial f(\psi)}{\partial \psi} \tag{3}$$

with the following boundary conditions on the surface ($z = 0$) and in the bulk phase:

$$k \frac{d\psi}{dz}\bigg|_{z=0} = \frac{\partial F_s}{\partial \psi}\bigg|_{\psi_s = \psi(z=0)}, \tag{4}$$

$$\lim_{z\to\infty} \psi(z) = \psi_b, \tag{5}$$

where ψ_b and ψ_s are the values of the order parameter in the bulk phase and on the surface respectively.

The first integral is

$$\frac{d\psi}{dz} = \pm \{2[f(\psi) - f(\psi_b)]/k\}^{1/2}. \tag{6}$$

The sign of the derivative is determined by the ratio of the values of ψ in the bulk phase and on the boundary: if $\psi > \psi_b$, then $d\psi/dz < 0$ and conversely. It follows from Eqns.(4) and (6) that

$$\frac{\partial F_s}{\partial \psi} = \pm \{2k[f(\psi_s) - f(\psi_b)]\}^{1/2}. \tag{7}$$

Hence one can find the order parameter on the surface ψ_s. If Eqn.(7) has several roots, then each of them leads to a definite spatial distribution of $\psi(z)$. The profile ensuring the minimum surface free energy σ corresponds to the condition for equilibrium:

$$\sigma = F_s + \int_0^\infty dz \left[k \left(\frac{d\psi}{dz} \right)^2 \right]. \tag{8}$$

Having specified a simple expression for F_s, it is possible to obtain a solution to Eqns.(3)–(5) in an analytical form and to analyse the possible situations. In the main, the following form of F_s is investigated:[20,23]

$$F_s = -\frac{1}{2} g \psi_s^2 - h_1 \psi_s. \tag{9}$$

It describes the perturbing influence of the wall on the semi-infinite system as a result of the modification of the chemical potentials of the components (second term) and the changes in the interactions between the molecules at the boundary (first term). The relation between the extrapolation length $\lambda = -k/g$ and the energy of the interaction of the sites in the surface layer J_s has been established with the aid of lattice models. Having characterised the difference between J_s and the energy of the interaction of sites in the bulk phase J by the quantity $\Delta_s = J_s/J - 1$, Mills[24] and Binder and Hohenberg[25] found $\lambda^{-1} = 1 - \Delta_s/\Delta_c$, where Δ_c is the critical value of Δ_s ($\Delta_c = 4$).[26]

We shall now consider the results obtained in the solution of Eqns.(3)–(5) and (9) for the simplest case where $h = h_1 = 0$ (Figs. 1 and 2). For fixed cohesion forces of the molecules in the surface layer Δ_s, it is always possible to differentiate in the phase diagram the temperature range in which the entire specimen is in a non-ordered state: $\psi(z) = 0$ (region V in Fig.1). For $\Delta_s < \Delta_c$ ($\lambda > 0$), this state persists until the attainment of the bulk-phase PT temperature. When non-zero values of the order parameter appear in the bulk phase, the substrate tends to disorder the system (region I), which diminishes $\psi(z)$ in the vicinity of the surface (Fig.2*a*). If the interaction energy of the molecules in the surface layer exceeds the critical value ($\Delta_s > \Delta_c$, $\lambda < 0$), the non-ordered state exists throughout the bulk of the specimen at temperatures $t > t_s > 0$. At t_s, order appears in the boundary layer of molecules (the C^1_{sur} surface transition takes place), but the non-ordered state of the substance persists away from the wall. Region II in the phase diagram (Fig.1) differentiates the states of the system for which the order parameter on the surface differs from the bulk-phase value but approaches

$\psi_b = 0$ on moving away from the boundary (Fig.2*b*). The decrease in temperature to the critical value induces a bulk phase transition (extraordinary C^{∞}_{ext} transition) and the establishment in region III (Fig.1) of the profile illustrated in Fig.2*c*. The boundaries of the ordinary (C^{∞}_{ord}), extraordinary, and surface transitions converge at a single point *Sp*, where $\Delta_s = \Delta_c$ ($\lambda^{-1} = 0$). The condition $\Delta_s = \Delta_c$ means that the presence of the wall does not influence the interaction energy of the molecules, so that, as a result of a special transition (*Sp*), the state of the system changes simultaneously throughout its bulk at the critical temperature. For $t < 0$, the distribution of the order parameter is shown in Fig.2*b*.

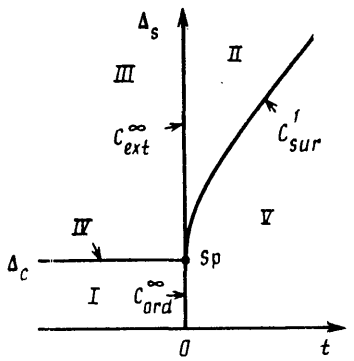


Figure 1. Schematic illustration of the phase transitions occurring in a semi-finite system[22] (for the explanation, see text).

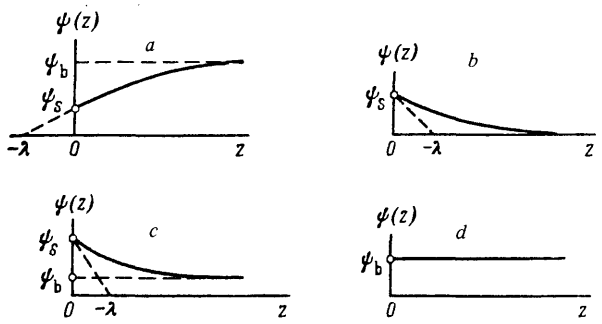


Figure 2. Variation of the order parameter ψ with the distance from the substrate surface for different values of the extrapolation length $\lambda = -k/g$ and temperatures t:[20] (a) $\lambda > 0$, $t < 0$; (b) $\lambda < 0$, $t > 0$; (c) $\lambda < 0$, $t < 0$; (d) $\lambda^{-1} = 0$, $t < 0$ ($h = h_1 = 0$ throughout).

Thus, even in the simplest case, the phenomenological theory makes it possible to discover a significant difference between the properties of the specimen in the bulk phase and in the surface layer. The nature of the transitions near the CP is controlled by the interaction energy of the molecules at the wall: an increase in Δ_s (and hence in g) increases the temperature of the surface transition and an order parameter different from the bulk-phase value appears above the critical temperature. The problem has been investigated in greatest detail in studies;[15,16,22,23] limitations on the values of the parameters h and h_1 were removed, non-classical temperature variations of the coefficients in Eqn.(1) were considered etc. More complex cases of semi-infinite systems with two order parameters have also been analysed.[27]

III. CAHN'S THEORY AND EXPERIMENTAL STUDIES ON WETTING TRANSITIONS

Consider a liquid consisting of components A and B with an upper consolute temperature (UCT). Above T_c, the liquid consists of a homogeneous phase with the composition φ_0 (concentration of component B). Below T_c, the mixture decomposes into the phases α and β, whose compositions φ_α and φ_β depend on temperature. We shall assume that phase β contains an excess of component B ($\varphi_\beta > \varphi_0$), whereupon phase α is enriched in component A ($\varphi_\alpha < \varphi_0$). As T_c is approached, the compositions of the phases coexisting at equilibrium approach one another and the interfacial tension at the $\alpha-\beta$ boundary diminishes. In the vicinity of T_c, simple scaling relations apply:[12,13]

$$\varphi_\beta - \varphi_\alpha \propto t^{\beta}, \tag{10}$$

$$\sigma_{\alpha\beta} \propto t^{\mu}, \tag{11}$$

where $\beta = 0.33$ and $\mu = 1.26$ are critical parameters. We now bring the mixture into contact with the wall, which adsorbs preferentially one of the mixture components (for example B). The behaviour of the two-phase system near the wall S is determined by the interfacial energies $\sigma_{\alpha s}$, $\sigma_{\beta s}$, and $\sigma_{\alpha\beta}$ at the S$-\alpha$, S$-\beta$, and $\alpha-\beta$ boundaries respectively. Under conditions where $\sigma_{\alpha s} - \sigma_{\beta s} - \sigma_{\alpha\beta} < 0$, the equilibrium wetting angle θ arises and Young's law holds:[28]

$$\sigma_{\alpha\beta} \cos\theta = \sigma_{\alpha s} - \sigma_{\beta s}. \tag{12}$$

In his analysis of the temperature variation of θ in the two-component system considered, Cahn[18] suggested that the difference between the interfacial energies ($\sigma_{\alpha s} - \sigma_{\beta s}$) in the vicinity of T_c is determined mainly by the compositions of the equilibrium phases and depends on temperature in the same way as $\varphi_\beta - \varphi_\alpha$. Then, taking into account Eqns.(10) and (11), we have from (12)

$$\cos\theta \propto t^{\beta-\mu}, \quad \beta-\mu = 0.93. \tag{13}$$

According to Eqn.(13), the condition for the complete wetting of the substrate surface by phase β ($\theta = 0$) is attained at a certain temperature T_W, which differs from the critical temperature. Then, when $T_c > T > T_W$, we have $\sigma_{\alpha s} - \sigma_{\beta s} - \sigma_{\alpha\beta} > 0$ and, for liquids with limited miscibility, contact with the wall by the component with the higher interfacial energy (A in the present instance) becomes unfavourable, which leads to the formation on the surface S of a layer of the phase in which the concentration of this component is lower.

The structure of the liquid at the substrate surface has been studied within the framework of the average field theory.[18] Here it is assumed that the microstructure produced in the liquid is controlled by the volume properties of the mixture, the concentration gradients, and the forces acting from the side of the wall only on the layer of molecules of the liquid adjoining it. The initial functional of the interfacial free energy has the form[18]

$$\sigma[\varphi] = F_s + \int_0^{\infty} dz \left[\Delta f(\varphi) + k\left(\frac{d\varphi}{dz}\right)^2 \right], \tag{14}$$

$$\Delta f(\varphi) = f(\varphi) - f(\varphi_0) - (\varphi - \varphi_0)\left(\frac{\partial f}{\partial \varphi}\right)\Big|_{\varphi=\varphi_0}, \tag{15}$$

where $f(\varphi)$ is the local density of the free energy of the homogeneous

liquid. The function $\Delta f(\varphi)$ reaches its minimum values for compositions corresponding to phase equilibrium [$\Delta f(\varphi_\alpha) = \Delta f(\Delta_\beta) = 0$] and has a local maximum at $\varphi_\alpha < \varphi < \varphi_\beta$. As the temperature approaches the critical value, $\Delta f(\varphi)$ at the local maximum diminishes and is very low in the vicinity of T_c.

The solution of the variational problem [Eqns.(14) and (15)] yields the spatial distribution of the concentration at the wall in each of the coexisting phases:

$$z(\varphi) = -\int_{\varphi_s}^{\varphi} [k/\Delta f(\varphi)]^{1/2}\, d\varphi. \qquad (16)$$

An elegant graphical analysis carried out by Cahn[18] established that near T_c the surface concentration φ_s is the same in both equilibrium phases and exceeds φ_β (the bulk phase concentration) for the more concentrated phase. Then, the function $\varphi(z)$ in phase α initially diminishes from φ_s *to* φ_β and at $\varphi = \varphi_\beta$ we have $\Delta f(\varphi_\beta) = 0$ and, according to Eqn.(16), $z \to \infty$, i.e. a macroscopic layer arises between the wall and phase α. Thus, a two-step transition is observed at the S$-\alpha$ interface: initially S$-\beta$ and then $\beta-\alpha$. When the temperature is appreciably below T_c, the adsorption of component B from phase α is slight and the condition $\varphi_s < \varphi_\beta$ holds. Since φ_s determines the lower integration limit in Eqn.(16), the profile of the variation of the concentration between the coexisting bulk phases β and α,[29] cut off at $\varphi = \varphi_s$, can be used to obtain the concentration profile $\varphi(z)$ at the S$-\alpha$ boundary. The transition from limited to complete wetting takes place at a definite temperature T_w and is a transition of the first kind.

The formation of a surface layer in which the concentration is close to φ_β is possible even in a homogeneous system for $\varphi_0 < \varphi_\alpha$ (under the conditions of the instability of the bulk phase having the composition φ_β). The difference from the two-phase system consists in the fact that the thickness of this layer is in this case finite, since $\Delta f(\varphi_\beta) \neq 0$.

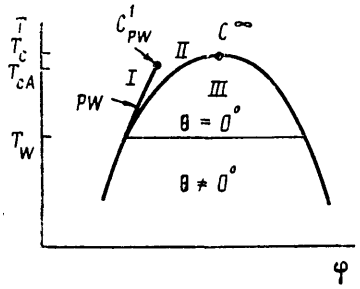


Figure 3. Phase diagram for a two-component semi-infinite system[18] (for explanation, see text).

The influence of the substrate on the two-component system is illustrated in the phase diagram in Fig.3. In the single-phase region I, the degree of adsorption of component B is low ($\varphi_s < \alpha_\beta$) and the composition of the surface layer never reaches φ_β even for $\varphi_0 = \varphi_\alpha$. Region II is one where the surface concentration exceeds the bulk phase concentration of component B in phase β. The appearance of a layer having a finite thickness with composition close to φ_β is characteristic of it. The *PW* line, separating these adsorption regions describes the concentrations of the homogeneous solution at which two profiles with different surface concentrations φ_s correspond to a single minimum in the functional (14). With increase in temperature the difference between these profiles diminishes and vanishes completely at the temperature T_{cA} at the critical point for the C^1_{PW} surface transitions (Fig.3).

Overall thermodynamic analysis[30] and the results of calculations based on different models[31–34] show that the *PW* line has a common tangent with the binodal curve at the point corresponding to the temperature T_W and the transition from the low adsorption region to the high adsorption region for systems having a UCT takes place on cooling. The deviation of T_{cA} from T_W varies from several to tens of degrees according to different estimates.[33–35] In region III (the region corresponding to complete wetting of the substrate), phase α is displaced from the surface of the wall by a macroscopic layer of phase β.

The strategy of the experimental studies of wetting transitions is determined mainly by the results of the theoretical analysis of the problem. The possibility of the appearance of wetting layers has been demonstrated already in the first study[36] of the influence of the substrate on the cyclohexane–methanol two-phase system (with a small amount of added water). The boundary with the non-critical phase (vapour) also played the role of a wall in the experiments.

Subsequent experimental studies of systems with a UCT [35,37–42] and systems with a lower consolute temperature (LCT),[43,44] carried out by various methods (visual observation,[37] capillary rise,[43] ellipsometry,[38–41] and light scattering[44] and reflection[42]), demonstrated convincingly that the formation of wetting layers is a general phenomenon associated with the influence of the surface of the wall. (The pattern arising under these conditions is illustrated schematically in Fig.4). The temperature of the transition from complete to limited wetting (T_W) differs significantly from the critical temperature. For systems with a UCT, it lies below T_c (for example, in the isopropyl alcohol–perfluoromethylcyclohexane system, $T_W = 38.0 \pm 0.1$ °C, while $T_c = 90.5° \pm 0.5$ °C [40]) and, for systems with a LCT, it lies above T_c (in the 2,6-lutidine–water system, $T_W \simeq 48$ °C, while $T_c = 34$ °C [43,44]).

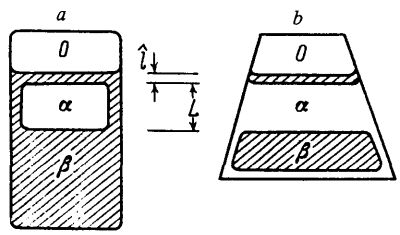


Figure 4. Experimentally observed wetting phenomena:[38] (a) methanol–cyclohexane system with added water in a glass bulb. The denser methanol phase β wets the glass surface and is distributed at the interface with the vapour 0; (b) the perfluoromethylcyclohexane–methylcyclohexane system in a quartz bulb. The lighter phase α with an increased methylcyclohexane contact wets quartz; the layer of phase β (enriched in C_7F_{14}) is distributed at the interface with the vapour.

Before considering experimental data referring to the measurement of the thickness of the wetting layers, we may note that Cahn's theory[18] was constructed without taking into account external fields.

Consequently, in the absence of the gravitational field, the wetting layer might be very thick and might occupy a considerable proportion of the volume of the system. In the gravitational field, the increased potential energy of the layer of the denser phase β at the interface with the vapour (Fig.4*a*) [or of the lighter phase α at the lower wall (Fig.4*b*)] tends to make it thinner. As a result of the balance between the gravitaional and surface forces, the equilibrium thickness of the layer $\hat{l}$ is attained. It follows from the analysis of the surface forces[45] that

$$\Pi(\hat{l}) = \Delta\rho g L, \qquad (17)$$

for $\pi(\hat{l})$ represents the forces acting per unit of each of the phases separated by a film; $\Delta\rho = \rho_\beta - \rho_\alpha$, ρ_α and ρ_β are the densities of phases α and β respectively, g is the acceleration in the free fall, and L is the thickness of the layer of phase α separating the wetting film and the bulk phase β (Fig.4).

If the attenuation of the wetting layer under the influence of the gravitational field is coupled with the rearrangement of the structure of the liquid owing to the overlap of the concentration profiles formed at the boundary of the film with the vapour and phase α, then $\pi(\hat{l})$ is determined by structural repulsion forces $\pi_c(\hat{l})$. Using the expression proposed by Widom,[46]

$$\Pi_c(\hat{l}) = \sigma' \exp(-\hat{l}/\xi), \qquad (18)$$

where ξ is the correlation radius of fluctuations in the bulk phase, we find that the thickness of the wetting film at the boundary with the vapour depends only slightly on the thickness of the layer of phase α but is extremely sensitive to temperature near T_c (by virtue of the temperature dependence of the correlation radius):

$$\hat{l} = \xi \ln\left|\frac{\sigma'}{\Delta\rho g L}\right|. \qquad (19)$$

Under conditions remote from T_c, where structural forces do not exert a decisive influence, the layer may be stabilised by long-range van der Waals forces:[47]

$$\Pi_м(\hat{l}) = W\hat{l}^{-q}, \qquad (20)$$

$$\hat{l} = \left(\frac{W}{\Delta\rho g L}\right)^{1/q}, \qquad (21)$$

where W is a coefficient which depends on the polarisabilities of phases α and β.[45] The exponent q reflects the presence or absence of a lag in the molecular forces: $q = 3$ for non-lagging forces and $q = 4$ for lagging forces.[45] Since the parameter W is proportional to the difference between the polarisabilities of the equilibrium phases, which depends on temperature in the same way as $\Delta\rho$,[47] the thickness of the wetting layers stabilised by molecular forces varies only slightly with temperature. The derivation of Eqn.(21) was based on a model in which the layer is assumed to be homogeneous up to its boundaries. The model inevitably breaks down and the thickness of the zone corresponding to the transition from the layer to the bulk phase is comparable to $\hat{l}$, which may occur when L is large and the thickness of the layer $\hat{l}$ is equal to several molecular diameters or if the width of the transition region, proportional to the correlation radius of the bulk phase fluctuations, increases as the temperature approaches T_c. In such cases there is a possibility of a transition from one stabilisation regime to another.[48] When $W < 0$ (attraction between the phases separated by a layer), only structural forces prevent the attenuation of the film. The final result depends on the balance between molecular, structural, and gravitational forces.

The thickness of wetting layers at the boundary with the vapour in systems having different chemical compositions (see Table) has been investigated by the ellipsometric method.[38–41] The results show that, below the wetting temperature, the thickness of the layer does not exceed 2 nm (in the *iso*-$C_3H_7OH - C_7F_{14}$ system[40,41]). Above T_W, the thickness of the layer reaches several tens of nm.

Studies over a wide temperature range indicate clearly the existence of two different mechanisms of the stabilisation of wetting layers. The role of molecular forces in the formation of wetting layers is manifested under conditions remote from T_c, where $\hat{l} \propto L^{-1/3}$ according to experimental data and small variations in thickness with temperature are observed. However, for large values of L, structural forces are apparently involved in stabilisation, which in fact leads to a weak dependence of the thickness on L (see Table, system 2). Near the critical temperature, where the zones corresponding to the transition from the film to the phases bounding it (the gas phase and phase α in Fig. 4*a*) begin to overlap, this is found

The thicknesses of the wetting layers at the interface with the vapour (experimental data).

No. of system	Layer	Second phase	T_c, °C	T, °C	L, mm	$\hat{l}$, mm	$-1/q$	Refs.
1*	C_7F_{14}	C_7H_{14}	46.0±0.2	23 45.27	6—22 3—10	7—40 70	1/3 0	[38]
2*	CH_3OH**	C_6H_{12}	50.8	room	8—200 >200	7—15 7	1/3 0	[38]
3*	CH_3OH***	C_6H_{12}	56.18	49—53	10	10—30	—	[39]
4	C_7F_{14}	iso-C_3H_7OH	90.5±0.5	38—50	2—20	35—45	0.06	[40 41]
5****	CH_3NO_2	CS_2	63.264	<60 60.264—63.064 63.064—63.114 63.114—63.263	8.2 8.2 8.2 8.2	400 400—600 600—200 200—800	— — — —	[42]

*The wetting transition temperature is below the freezing point of the mixture.
**The water content in the system is 0.4%.
***The water content in the system is 0.333%.
****At the interface with glass.

to be the decisive factor which regulates the temperature variation of the thickness of the [wetting?] layer[39,42] and ensures the absence of a dependence on the thickness of the layer of phase α. The formation of thick wetting layers of the polar nitromethane from a nitromethane–carbon disulphide mixture on a horizontal glass surface can hardly be accounted for by the stabilising action of dispersion forces. On the other hand, calculations of the Hamaker constant performed[49,50] for this system on the basis of the Dzyaloshinskii–Lifshits–Pitaevskii theory[51] have shown that dispersion forces tend to destabilise the layer of nitromethane on the glass surface. The existence under equilibrium conditions of layers hundreds of nm thick requires the presence of forces acting over long distances. It has been suggested[49,50] that, in the presence of a polar component (nitromethane), having a high dielectric constant, the hydroxy-groups dissociate on the glass surface and the resulting electrostatic forces are involved in the stabilisation of the layer. How correct this model is will be shown by studies with careful monitoring of the surface charge.

The pronounced discrepancies between the thicknesses of the wetting layer measured experimentally and calculated using the theory of dispersion interactions[51] for certain systems[52] require the estimation of the time intervals necessary for the attainment of equilibrium. Such an estimate has been made[52] for two mechanisms of the variation of the thickness of the layer—diffusion of the mixture components to the interface and the leakage of the liquid from the layer via channels formed by the wetting layers on the surface of the vessel walls. If the growth of the layer is regulated by the diffusion of the components, then under conditions remote from T_c, the formation of the equilibrium wetting layer from liquids with limited miscibility on the surface of the substrate takes days and even months. As T_c is approached, the time required for the attainment of equilibrium increases. In a stirred system, this time is shortened but the thickness of the layer increases with increasing rate of stirring, which indicates a quasi-equilibrium state of the layer. If the equilibration mechanism in the attenuating layer is determined by the flow of liquid, then the equilibration time depends on the width of the channel and may amount to years.

A number of facts which cannot be explained within the framework of the above theoretical considerations have been discovered experimentally: a weak dependence of $\hat{l}$ on the thickness of the upper phase in the isopropyl alcohol–perfluoromethylcyclohexane (PFMCH) system (Table, system 4) and the decrease in the thickness of the wetting layer near T_c.[39,42] The results of a study of the phenol–water system are fairly unexpected from the theoretical point of view.[53] Expecting to observe a thick layer of phenol in the two-phase region at the boundary with the vapour, the authors[53] observed instead the appearance of hundreds of tiny drops which exist near the boundary for a long time.

Furthermore, studies on the wetting transitions in different systems have shown that the attainment of the critical temperature is not always accompanied by the formation of wetting layers. There are no layers at the boundary with the vapour in the cyclohexane–methanol two-component system[39] (only the addition of small amounts of water initiates transitions at the suface). This is clearly manifested in experiments on the wetting of solid substrates. Thus the temperature of the wetting transition on the glass surface in the 2,6-lutidine–water system diminishes, approaching T_c, with increase in the concentration of potassium chloride.[54] At the salt concentrations in excess of 0.072 M, the transition is suppressed and there is only limited wetting of the glass by the phase enriched in lutidine.

Glass capillaries whose surface has been methylated to different extents have been used[55,56] to investigate the wetting transitions in the nitromethane–carbon disulphide system. On a weakly methylated surface, the approach to the critical temperature is accompanied by wetting transitions of the first kind. However, when the polarity of the substrate diminishes so much that the preferential adsorption of carbon disulphide begins, the wetting transition vanishes over the entire temperature range below T_c and limited wetting of the capillary surface by the carbon disulphide phase takes place. Measurements of the wetting angle θ on glass in the systems cyclohexane–methanol with small amounts of added water, cyclohexane–aniline, and ethyl salicylate–diethylene glycol[57] have shown that in the vicinity of T_c the angle θ reaches 90°. The experimental data presented show that Cahn's theory[18] does not exhaust the entire wide variety of situations arising in real systems. The restriction of the zone where the substrate exerts an influence to direct wall–liquid contacts is an extremely controversial postulate of the theory.

The question of the existence on the phase diagram of a line separating the regions corresponding to strong and weak adsorption of one of the components also requires careful experimental confirmation (Fig.3). An attempt has been made[35] to observe a jump in the adsorption of PFMCH from an isopropyl alcohol–PFMCH mixture at the boundary with the vapour. When the homogeneous mixture was cooled slowly, the ellipticity coefficient of the light reflected from the liquid–vapour surface increased sharply. It was coupled with the appearance of a PFMCH film. Thick films are formed and persist indefinitely at a temperature higher by 0.18 K than the phase transition temperature in the bulk phase. However, when the cooling of the system was interrupted by vigorous shaking and subsequent standing until equilibration, this effect was absent. Consequently, in this instance there is no abrupt change in the degree of adsorption. The size of monodisperse spherical quartz pellets in the lutidine–water single-phase system has been measured[44] by the light scattering method as a function of the mixture composition and temperature. Having observed an increase in the intensity of the scattered light as the lutidine concentration approaches the value corresponding to the coexistence curve, the authors[44] postulated that this is due to the increase in the thickness of the adsorption layer of lutidine on the surface of the particles of the dispersion phase. It was also established that a decrease in the lutidine concentration in the mixture entails the aggregation of the particles. The curve corresponding to the aggregation of the particles on the phase diagram for this system was identified with the *PW* line.

IV. GENERALISED PHASE DIAGRAMS AND SURFACE SPINODAL CURVES

The place occupied by the phenomena involving wetting and the formation of a layer with a finite thickness in the overall pattern of the influence of the surface on PT is clearly defined by the phenomenological theory.[23] The inclusion of the $h\psi$ and $h_1\psi_s$ terms in Eqns.(1) and (9) for the free energy density and the direct contact energy made it possible to construct diagrams for the transitions in the space of the variables $\{t, h, h_1, g\}$.[23] Fig.5 presents the results obtained for the three previously differentiated regions based on different values of the parameter g. It follows from the functional (2) and Eqns.(1) and (9) that, when the signs of the parameters h and h_1 are changed, the quantities F, $f(\varphi)$, and F_s retain their values when ψ is replaced by $-\psi$. This means that, in the vicinity of the critical temperature, all the effects associated with the influence of

the wall and described previously for one of the equilibrium phases ($h = 0$) should be reproduced also for the other phase when the sign of the parameter h_1 changes, i.e. the wetting of the wall by one of the phases should always be observed in the vicinity of T_c. The principal characteristics of the phase diagrams for semi-infinite systems are illustrated in Fig.5: the wetting transitions for phase β (and correspondingly for phase α) at $h = 0$ are represented by the $W(D)$ lines, the set of points corresponding to the sharp change in the thickness of the adsorption layer in the single-phase system forms the $PW(PD)$ surface bounded by the loci of the critical points $C^1_{PW}(C^1_{PD})$. The character of the variation of the wetting lines for small deviations of the temperature from the critical value is described by the power relation $|t| \propto |h_1|^{1/\Delta_1}$, where $\Delta_1 = 1/2$, 1, and 3/2 [23] for $g < 0$, $g = 0$, and $g > 0$ respectively. For $g > 0$, the C^1_{PW} and C^1_{PD} lines extend to $t > 0$, meeting at the surface transition point C^1_{sur} (Fig.5*c*). The positions of the ordinary (C^∞_{ord}), special (Sp), and extraordinary (C^∞_{ext}) transitions (Fig.1) are illustrated in Fig.5 by multicritical points at which the lines of different PT intersect.

The jump in the thickness of the layer adjoining the substrate (to which the PW line in Fig.3 corresponds) may be regarded as a surface transition of the first kind. Since the existence of metastable and unstable states is associated with such transitions, then, by analogy with the PT in the bulk phase, in describing the sharp change in the thickness of the layer one may introduce the concept of the "surface" spinodal curve. The position of the surface instability curve relative to the PW line and the coexistence curve for the bulk phases has been analysed in detail.[32] It has been shown that the branches of the spinodal curve originate from the critical point C^1_{PW} and their positions on the phase diagram depend significantly on the ratio of the interaction energies of the components in the bulk phase of the system and on the surface of the substrate (Fig.6). For example, for $g < 0$, both branches of the spinodal curve terminate at the coexistence curve, the left branch being located under these conditions very close to the PW line (Fig.6*a*). It has been suggested[32,58] that the line, which is a continuation of the spinodal curve into the two-phase region of the bulk of the system, characterises the boundary of the wetting instability. According to this hypothesis, the substrate is wetted in the metastable region after the intersection of the surface spinodal curve, provided that the system was initially in the weak adsorption region and that the transition from one region in the phase diagram to the other was rapid. (If the initial state corresponds to the region with strong adsorption, wetting is observed under the conditions corresponding to the coexistence curve.) On this basis, the hypothesis was put forward that the surface of the substrate may be wetted in the two-phase region below T_W when the system passes rapidly to the region of surface instability.[32] Thus one should expect in the two-phase region a qualitatively different behaviour of the system in the vicinity of the surface of the substrate depending on the initial state and the rate of cooling. The processes occurring at the wall can compete with the initiation of the new phase in the bulk of the system. This occurs when the state of the system in the bulk phase is metastable, being stable with respect to infinitesimal changes in composition, while near the substrate surface it is unstable, i.e. unstable in relation to infinitesimal fluctuations. One can then observe the segregation of a phase from the metastable state via a barrier-free mechanism.

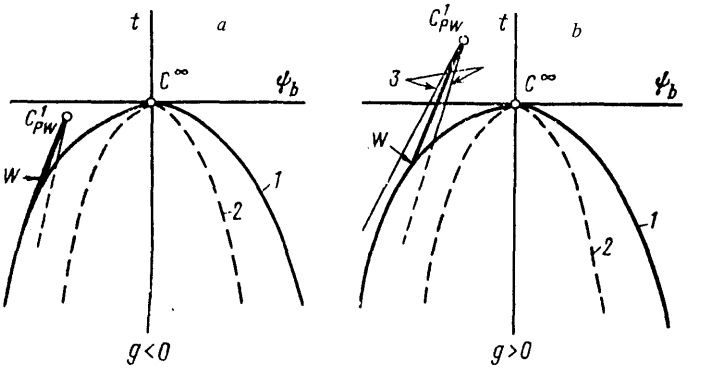


Figure 6. Phase diagram for a semi-infinite system in terms of the coordinates volume order parameter (ψ_b) – temperature (t);[32] 1) coexistence curve; 2) spinodal curve; 3) surface spinodal lines. For the significance of other notation, see the caption to Fig.5.

We shall consider next a generalised phase diagram corresponding to the case where the energy of the interaction between the molecules in the surface layer is smaller than in the bulk phase (Fig.5*a*). Calculations have shown[23] that, for certain values of the parameters h_1 and g, the transition from limited to complete wetting on moving along the coexistence curve may take place continuously and not as a result of an abrupt change in the thickness of the surface layer.

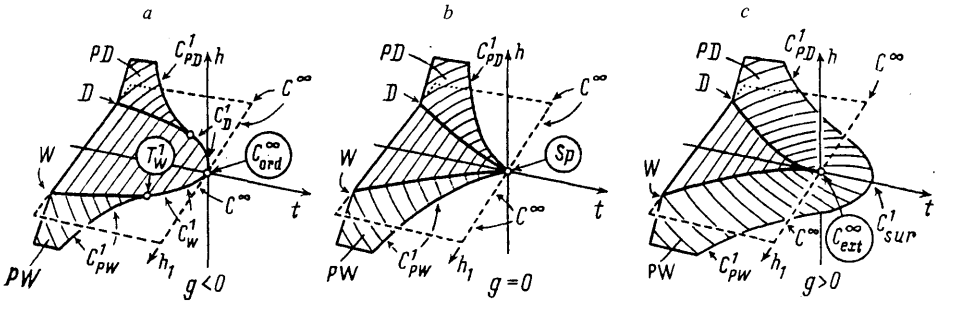


Figure 5. Phase diagram for a semi-infinite system for different values of the parameter g;[23] W, D—wetting lines; C^1_W, C^1_D—critical wetting lines; PW, PD—surfaces separating the regions with weak and strong adsorption; C^1_{PW}, C^1_{PD}—the critical point loci bounding the region; C^1_{sur}—surface transition point; C^∞—line corresponding to the transition in the bulk phase; multicritical effects are indicated within circles.

Such a transition is called a critical wetting transition (the C_W^1 and C_D^1 lines correspond to this transition in Fig.5*a*). The tricritical wetting point T_W^1 separates the W and C_W^1 transitions. The locus of the critical points C_{PW}^1 of the transition associated with the abrupt change in adsorption in single-phase systems (in systems where critical wetting takes place, PW transitions are not observed) terminates at the point T_W^1. Fig. 5*a* shows that the critical wetting occurs when $|h_1| < |h_{1,T_W^1}|$ (with increase in g, $|h_{1,T_W^1}| \to 0$). Consequently, this transition can be observed only in systems with low values of the parameter h_1.

The possibility of the continuous growth of the thickness of the wetting layer under the conditions of coexistence of the bulk phases was first pointed out in studies[59,60] where the wetting transitions were analysed using one-component liquid models. It was shown[59] that, in the critical wetting transitions, the following relation should hold for the interfacial energies:

$$\sigma_{\alpha s} - \sigma_{\beta s} - \sigma_{\alpha\beta} = -C\left(1 - \frac{T}{T_{cW}}\right)^2,$$

which leads to a temperature dependence of the wetting angle differing from the scaling relation (13):

$$\cos\theta = 1 - \frac{C(1 - T/T_{cW})^2}{D(1 - T/T_c)^{1.26}},$$

where C and D are constants and T_{cW} is the critical wetting transition temperature.

The experimental data[35,36,40,41,43,44,54–56] leave no doubt that the first order wetting transition does indeed exist. On moving along the coexistence curve, the degree of adsorption changes abruptly at some instant, becoming (in the absence of external fields) infinite. The possibility of a continuous transition is less evident. Theoretical analysis of specific systems may be of great help in selecting systems in which one should seek critical wetting transitions. As an example, we may refer to a study[61] where wetting transitions were investigated taking into account the orientation of the molecules on the substrate surface. The authors[61] observed an alternation of wetting transitions on moving along the binodal curve towards T_c. Polymer systems must also be included among specific systems: for virtual constancy of the segment–segment and segment–substrate interaction energies in such systems, it is possible to alter significantly the concentration and temperature ranges where wetting transitions may occur by varying the chain length within wide limits.

V. PHASE TRANSITIONS IN SEMI-INFINITE POLYMER SYSTEMS

Numerous theoretical and experimental studies have been devoted to questions of the adsorption of polymers.[62–66] We shall concentrate attention on the investigation of the concentration profile of polymer segments in a poor solvent, following Cahn's ideas[18] and on the basis of the results of a number of studies.[32,67–70] We shall assume that the polymer concentration on the surface is low ($\varphi_s = \lim_{z\to 0}\varphi(z)$, $\varphi_s \ll 1$), which makes it possible to neglect the interaction between the segments of the macromolecules in the first layer and to represent F_s in the form

$$F_s = \sigma_0 + \sigma_1\varphi_s, \qquad (22)$$

where σ_0 is the surface energy at the substrate–solvent interface; $\sigma_1 > 0$ corresponds to an increase in energy with increasing concentration and indicates that the interaction of the macromolecule with the substrate is unfavourable. If the adsorption of the macromolecule reduces the free energy of the system ($\sigma_1 < 0$), then the condition $\varphi_s \ll 1$ holds only for weakly binding substrates: $|\sigma_1| < k_BTa^{-2}$.[69,70]

Under ideal equilibrium conditions, the concentration profile $\varphi(z)$ is determined from the minimum in the functional

$$\sigma - \sigma_0 = -|\sigma_1|\varphi_s + \int_0^\infty dz\left[f(\varphi) - \mu\varphi + \pi + \frac{k_BT}{24a\varphi}\left(\frac{d\varphi}{dz}\right)^2\right], \qquad (23)$$

where

$$f(\varphi) = k_BTa^{-3}(\varphi N^{-1}\ln\varphi - v\varphi^2/2 + w\varphi^3/6)$$

is the local free energy density (in terms of a virial expansion) of the polymer solution,[8] a the size of the site in the Flory lattice,[7] N the number of units in the polymer chain, and v and w are parameters describing the pair and three-particle interactions between segments respectively. For v greater than the critical value v_c, it is possible to differentiate on the phase diagram a concentration range in which the formation of two phases with different polymer concentrations ensures a minimum in the free energy of the system. The functional (23) has been analysed in detail[67,68] in relation to a range of low polymer concentrations in a poor solvent. In this case, the osmotic pressure π of the macromolecules in solution is very low and one can assume that $\pi \simeq 0$ and that the chemical potential is large: $\mu \simeq k_BTa^{-3}N^{-1}\ln\varphi_0$. The introduction of the variables $\gamma = 6|\sigma_1|\cdot a\xi/k_BT$, $y = (\varphi/\varphi_\beta)^{1/2}$, $x = z/\xi$, and $\eta^2 = [\ln(\varphi_0/\varphi_\beta) + 1]/\ln\varphi_\alpha$ makes it possible to represent the functional (23) in the form

$$\frac{\sigma - \sigma_0}{|\sigma_1|\varphi_\beta} = -y_s^2 + \gamma^{-1}\int_0^\infty dx\left[y^6 - 2y^4 + \eta^2y^2 + \left(\frac{dy}{dx}\right)^2\right], \qquad (24)$$

where ξ is the correlation radius of the concentration fluctuations in solution for $\varphi_0 = \varphi_\beta$ and φ_α and φ_β are the equilibrium compositions of the dilute and concentrated phases respectively.

Next we obtain from the scheme described in Section II

$$\left(\frac{dy}{dx}\right)^2 = y^6 - 2y^4 + \eta^2y^2, \qquad (25)$$

$$-2y_s = \frac{2}{\gamma}\left(\frac{dy}{dx}\right)\Big|_{x=0} = -\frac{2}{\gamma}(y_s^6 - 2y_s^4 + \eta^2y_s^2)^{1/2}. \qquad (26)$$

It follows from Eqn.(26) that the real surface concentrations y_s can be obtained if the condition $1 - \eta^2 + \gamma^2 \geqslant 0$ is satisfied. Since η^2 is determined by the concentration of the solution, the length of the polymer chain, and temperature, it follows that, for a specified value of η, one can select substrates for which $\gamma \gg \gamma^* = (\eta^2 - 1)^{1/2}$ and $\varphi_s/\varphi_\beta = y_s^2 \simeq 1 + \gamma$, i.e. near the wall the concentration of the segments corresponds to a semidilute solution of the polymer and the "tail" of the profile extends into the bulk phase where the concentration is low. (For $\gamma < \gamma^*$, the energy of the interaction of the macromolecule where the substrate surface is low and cannot compensate for the energy expenditure on the creation of the concentration gradient, adsorption is an energetically unfavourable process.)

Detailed consideration of the density profile of the segments near the substrate surface[67,68] established that, over small distances $z < \xi$, the distribution of the concentration is determined solely by the energy of adhesion of the segments to the surface and that, for $\gamma \gg \gamma^*$, the concentration of the segments falls rapidly on moving away from the substrate. The distribution of the concentration in the central and "tail" parts of the profile depends significantly on η.

For $\eta^2 < 9/8$, a point of inflexion appears on the concentration profile and a fairly extended plateau is formed. The width of the plateau increases as the bulk-phase concentration of the polymer solution approaches values corresponding to the coexistence curve. For long distances from the substrate surface, the concentration of the segments tends exponentially towards the bulk-phase value. Thus the relations discovered in the study of the influence of the surface on homogeneous systems near the critical temperature[18] were also manifested in polymer solutions.

By expanding the local free energy density near T_c in series in terms of the order parameter $\psi = (\varphi - \varphi_c)/\varphi_c$, the functional of the free energy of the polymer system was transformed[32] into a form which has been investigated in detail within the framework of the phenomenological theory. For a polymer solution, we have

$$F_p[\psi(z)] = D^{-1}N^{-1}\left\{\int_0^D \mathrm{d}z\left[\frac{a^2}{24}N^{1/4}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + \right.\right.$$
$$\left.\left. + \frac{1}{2}\left(\frac{\chi_c - \chi}{\chi_c}\right)\psi^2 + \frac{1}{12}N^{-1/4}\psi^4 - h\psi\right] - h_1\psi_s - \frac{1}{2}g\psi_s^2\right\}. \quad (27)$$

In the case of a polymer blend with equal sizes of chains of different kind, we have the expression

$$F_{cm}[\psi(z)] = D^{-1}N^{-1}\left\{\int_0^D \mathrm{d}z\left[\frac{a^2}{24}N\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + \right.\right.$$
$$\left.\left. + \frac{1}{2}\left(\frac{\chi_c - \chi}{\chi_c}\right)\psi^2 + \frac{1}{12}\psi^4 - h\psi\right] - h_1\psi_s - \frac{1}{2}g\psi_s^2\right\}. \quad (28)$$

In Eqns.(27) and (28), χ is the Flory–Huggins parameter,[7] χ_c is the value of χ at the critical point, and $D \to \infty$.

Thus the results of the study of the influence of the substrate surface on the phase transitions in immiscible liquids can be extended also to polymer systems. The presence of larger multipliers before the gradient terms in Eqns.(27) and (28) ($N^{1/2}$ and N respectively) compared with Eqn.(2) does not alter qualitatively the results presented in Figs.5 and 6. All the features discussed in Sections III and IV are retained on the phase diagrams of semi-infinite polymer systems. They reflect the possibility of wetting, of the transition from weak to strong adsorption in the single-phase region, and of the existence of surface spinodal curves and the associated wetting in the metastable region of the bulk of the system at a temperature below T_W. We may note that, in contrast to binary liquid mixtures for which the metastability limit is hardly attainable experimentally,[71] in polymer systems (and especially in polymer blends[72,73]) a labile state is really observed for large macromolecules ($N \to \infty$). If an analogous systems arises also in wetting polymer films, then there is a possibility of the experimental observation of the metastable and unstable wetting states.

Only the temperature range near the critical value was investigated by Nakanishi and Pincus,[32] but the parameter h_1 selected was too large, which led to the conclusion that critical wetting cannot be observed in polymer systems. The problem of the wetting of the substrate surface by polymer blends has been analysed in detail.[74] We shall consider the conditions for the occurrence of critical wetting. As we have seen above, a wetting transition of the second kind occurs when, on moving along the coexistence curve from the region of low miscibility of the components, the surface concentration increases continuously and reaches the concentration of the wetting phase. Since the region in which critical wetting occurs is bounded by the tricritical wetting point (Section IV and Fig.5*a*), it is possible to determine the concentration of the blend $\varphi_{T_W^1}$ at which the conditions $\partial^2\sigma/\partial\varphi_s^2 = 0$ and $\varphi_s = \varphi_\beta$ hold simultaneously. For a mixture of macromolecules with $N_A = N_B = N$, it was found that[74]

$$\varphi_{T_W^1} \cong -\frac{a}{g(18N)^{1/4}}. \quad (29)$$

The condition $\varphi_s = \varphi_\beta$ indicates a planar concentration profile near the substrate surface ($\mathrm{d}\varphi/\mathrm{d}z|_{z=0} = 0$). Consequently the parameter h_1 at the point T_W^1 can be estimated from Eqns.(4), (9), and (29):

$$h_{1,T_W^1} = -g\varphi_s = -g\varphi_\beta = -g(1 - \varphi_{T_W^1}) \approx -g + a(18N)^{-1/4}.$$

Then, a wetting transition of the first kind always appears for $h_1 > h_{1,T_W^1}$ and $\varphi < \varphi_{T_W^1}$, while a continuous transition is possible for $h_1 < h_{1,T_W^1}$ and $\varphi_{T_W^1} < \varphi < \varphi_c$. By altering the concentration along the branches of the binodal curve, we find the critical wetting condition for a fixed values of $h_1 < h_{1,T_W^1}$:[74]

$$\varphi_{cw} = 1 + h_1/g.$$

Thus polymer blends are good objects for the observation of critical wetting, since, by altering the chain length, it is possible to vary h_{1,T_W^1}.

Despite the considerable progress in the theoretical analysis of the problem, there have been no complete experimental investigations of wetting transitions in polymer systems. There are literature data indicating the appearance of thick adsorption polymer layers in adsorption from a poor solvent.[62,63] The adsorption of poly(methyl methacrylate), polystyrene, and their copolymers from a mixture of carbon tetrachloride (an effective solvent) and heptane (a non-solvent) on quartz particles has been investigated in fair detail.[75] With increase in heptane concentration near the limit of stability of the homogeneous solution, a sharp increase in the adsorption of polystyrene copolymers with a high styrene content was observed. There was a parallel variation also of the volume of the deposit of the disperse phase particles. These factors indicate the formation of extended adsorption layers on the surface of the quartz particles. The influence of temperature on the adsorption of the polymer near the phase transition point in the bulk of the polystyrene–cyclohexane system has been investigated.[76] The appearance of a peak on the temperature variation of the ellipticity coefficient of the light reflected from the solution–vapour boundary at polymer concentrations above the critical value was attributed[76] to the formation of a wetting film of the solvent. The examples quoted confirmed to some extent the results of the theoretical consideration of the problem. At the same time, systematic investigations of the wetting phenomena arising under PT conditions in the bulk of polymer systems have still to be carried out.

An important application of the theory discussed above involved the calculation of the interaction forces between surfaces coated by adsorption layers of macromolecules. An undoubted advantage of the theory consists in the fact that all the data necessary for the calculations (information about the sizes of the unperturbed polymer chains, adsorption, and the concentrations of the equilibrium phases) can be obtained by studying the volume properties of the solution. Such calculations have been performed[68] for the specific polystyrene–cyclohexane system and have been compared to the results of an experimental study of the interaction forces between mica plates coated by adsorption layers of polystyrene in cyclohexane.[77,79] It was found that the calculations reproduce satisfactorily the experimentally observed inhomogeneous character of the variation of the forces and make it possible to estimate the distances over which attraction between the plates begins to be manifested and is then replaced by repulsion. Since the profile of the forces is a reflection of the distribution of the concentration of the chain segments near

the substrate surface, it follows that attraction over a distance exceeding the size of the unperturbed polymer coil arises as a consequence of the increase in the polystyrene concentration in the zone corresponding to the overlap of the concentration profiles up to values in the range $\varphi_\alpha < \varphi < \varphi_\beta$. In this case, strong interactions between segments of the adsorbed chains, characteristic of the two-phase region of the system, take place, and the plates attract one another. When the plates have shifted so much that φ becomes greater than φ_β, the attraction is replaced by repulsion. Although fine details of the forces profile are fairly satisfactorily predicted by the theory, there is no complete agreement between the absolute values of the forces. This is probably because of the neglect of the possibility of the formation of bridges as a result of the binding of the macromolecule to both plates (it has been shown[80] that the formation of a small number of bridges can become the main source of the interaction between the adsorption layers).

The theory of PT in semi-infinite polymer solutions creates a satisfactory basis for the discussion of the extensive experimental data[81] on interfacial adsorption layers whose stability is fairly high, which has in fact been demonstrated.[82] We shall consider the phase diagram of a polymer solution (Fig.7), in which a boundary between regions differing in the degree of adsorption of the polymer (*PW*) and the gel formation region (shaded) was observed. Suppose that the surface activity of the polymer is fairly high so that $\varphi_s > \varphi_g > \varphi_0$ (φ_g is the concentration at which gel formation takes place). If the concentration of the solution is lower than the values corresponding to the *PW* line, the degree of adsorption is low, but as soon as the concentration exceeds these values, the degree of adsorption becomes high ($\varphi_s > \varphi_\beta$) and a plateau appears on the concentration profile [where $\varphi(z) \simeq \varphi_\beta$], whose extent increases as φ_0 approaches φ_α. If the concentration on the plateau exceeds the gel formation concentration, then a film of gel arises at the interface. The thickness of this film corresponds to the width of the plateau and in the vicinity of φ_α greatly exceeds the size of the unperturbed polymer coil.

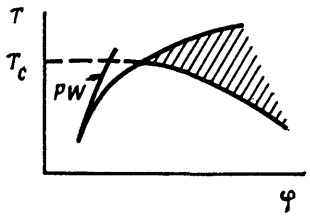


Figure 7. Phase diagram for a semi-infinite polymer solution.[82] The composition region in which gel formation takes place is shown shaded.

VI. THE ROLE OF LONG-RANGE FORCES IN WETTING TRANSITIONS

The theories of the surface transitions in semi-infinite systems considered were constructed taking into account surface forces with a small radius of action. This approach presupposes the existence of a non-specific dependence of the contact energy F_s on the composition of the surface layer and precludes an adequate description of real systems in which the zone of action of surface forces is known[45,83] not to be restricted to a monolayer. The approach to real conditions requires the analysis of the long-range action of the substrate. At the present time, theoretical studies have been carried out on continuous,[33,84–90] lattice,[31,60,91–95] and effective models of the layer.[96–100] Surface transitions in one-component systems and binary liquid mixtures are discussed within the framework of these models. An important aspect of such studies is the search for a relation beween the parameters of the microscopic interactions occurring in the system and the type of the surface transition. The introduction of the potential of the interaction between molecules in the bulk phase makes it possible to remove the limitation associated with the gradient form of the local free energy density and to describe the properties of the inhomogeneous liquid by considering the interaction occurring at the molecular level.

Careful analysis of this question, resorting to different models, showed that the type of the wetting transition is extremely sensitive to the form of the pair interaction potential. When the attraction of the molecule by the wall and by the surrounding molecules is described by potentials which decrease exponentially with increase in the distance between them, one can observe the appearance of wetting transitions of the first and second kind.[84,85] If the attraction between the molecules in the bulk phase operates over distances greater than the surface forces, a transition of the first kind occurs; otherwise we have a transition of the second kind (critical wetting). This model has been investigated in detail.[87] Much attention has been devoted to the modelling of the interactions in the system using the Lennard-Jones potentials.[31,60,85,86,89,90,101] In this case only a wetting transition of the first kind occurs and the features characteristic of it appear. It is noteworthy that the specific features of the microscopic interactions are manifested in the laws according to which the thickness of the layer increases as the system approaches saturation: $\hat{l} \propto |\ln|\Delta\mu||$ for forces with a small radius of action and $\hat{l} \propto |\Delta\mu|^{-1/3}$ for long-range forces.[31]

The interaction potentials between the molecules of the liquid and the substrate $V(z)$ and between the adsorbed molecules and the bulk of the liquid $U(z)$ have been described[89,93–96] by a more general expression

$$V(z) = -\left[\sum_{i=3}^{M} \gamma_{wi}/z^i\right], \quad U(z) = -\left[\sum_{i=3}^{M} \gamma_{fi}/z^i\right].$$

Depending on the coefficients γ_{fi} and γ_{wi}, in these systems it is possible to differentiate critical wetting, a wetting transition of the first kind, and other types of surface transitions. The important role of the terms γ_{f4}/z_4 and γ_{w4}/z^4 in the occurrence of critical wetting has been demonstrated in a study,[96] where an analytical expression was obtained for the separatrix separating the regions of the first- and second-order wetting transitions. The results[89,90,93–96,102] have shown that the fine details of the microscopic interactions are reflected in the macroscopic behaviour of the semi-infinite system: whether or not the wetting layer grows continuously or abruptly with increase in temperature and as the latter approaches T_c depends on the many-particle interactions and the structure of the substrate. Naturally, it follows from some of the above studies[89,94,96] that, in order to be able to predict the type of transition in each specific system, it is essential to have detailed information about it and the determination of such information constitutes an extremely complex problem. In their turn, experimental studies of the wetting transitions can prove an extremely valuable source of information about the microscopic interactions.

Next we shall consider, on the basis of the results of a number of studies,[21,91,92,103,105] what new contributions are made by long-range forces, compared with the forces with a small radius of action, to the

wetting transitions. As we have demonstrated above, in the latter case the presence of the substrate always initiates wetting in the vicinity of the critical temperature. We shall compare the phase diagrams presented in Fig.5 with the diagrams constructed[91,92] on the assumption that weak long-range forces exist, diminishing on moving away from the substrate surface in accordance with the law $h_{LR} \propto z^{-(m+1)}$ (where $m = 2, 3$), and there are short-range interaction forces between the molecules of the liquid (Fig.8). We shall assume that these forces promote the wetting of the substrate by phase β for $h_1 > 0$. The diagrams have many features in common: they reflect the presence of ordinary, special, and extraordinary transitions determined by the effective parameters of the interaction of the molecules of the liquid at the wall g^*; the type of behaviour of the wetting lines near T_c is the same. However, significant differences are also manifested. Fig.8 shows that, near T_c for $h_1^* < 0$ and $g^* = 0$, and $g^* > 0$, the wetting transitions, which in the case of short-range forces of the interaction of the substrate are characterised by the formation of a wetting layer (phase α) of infinite thickness (in the absence of gravitational field), now become transitions accompanied by the appearance of layers having a finite thickness (*PD*). Furthermore, for $g^* < 0$, the critical wetting transitions are transformed into wetting transitions of the first kind and the wetting of the substrate by the second phase is fully suppressed.

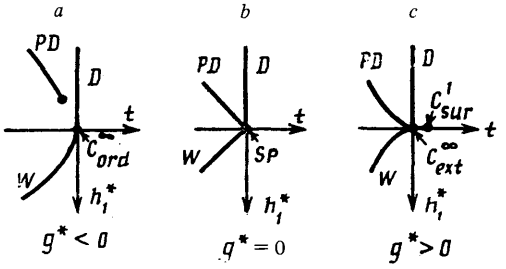


Figure 8. Phase diagram for a semi-infinite system with weak long-range forces in the substrate[92] (the legend is given in the caption to Fig.5 and further explanation can be found in the text).

The breakdown of the symmetry of the phase diagrams, characteristic of short-range potentials of the substrate (Fig.5), can find an explanation within the framework of the phenomenological theory if account is taken of the long-range effect of the substrate by including in Eqn.(2) the term[21,91,92,103–105]

$$\int_0^l [-h_{LR}(z)\,\psi(z)]\,dz, \quad l \to \infty .$$

This leads to an additional change in the interfacial free energy by the amount $\Delta\sigma = Al^{-m}$. Next, if the long-range forces cooperate with the forces of the direct interaction of the liquid molecules with the wall, then, for $h_1 > 0$, $\Delta\sigma$ is positive and the formation of a wetting layer with an infinite thickness ($l = \infty$) ensures a minimum in the free energy of the system. In this situation a macroscopic layer arises only as a result of a transition of the first kind. On the other hand, if the interactions of the substrate with the nearest layer of molecules are favourable for the other phase ($h_1 < 0$), then $\Delta\sigma < 0$ and at $t \neq 0$ the macroscopic layer of this phase never corresponds to the conditions for a minimum in the interfacial free energy, i.e. the long-range forces suppress the wetting transition. In this case critical wetting occurs at T_c.

The inhibition of the wetting transitions by long-range forces makes it possible to understand the results of experimental studies in which there was no wetting in the vicinity of T_c. On the basis of the phase diagram illustrated in Fig.8*a*, Franck and co-workers[55,56] interpreted the results of the study of such transitions in the nitromethane–carbon disulphide system on a chemically modified glass surface. It was assumed that, with increase in the number of methyl groups on the surface, the parameter h_1 diminishes monotonically, while the sign of the long-range potential of the substrate remains unaltered. The experimentally observed increase in the wetting transition temperature and its approach to the critical temperature with decrease in the polarity of the glass can then be accounted for with the aid of the phase diagram in Fig.8*a*. Indeed, when $h_1^* \to 0^+$, then we also have $t_W \to 0$. If the degree of modification of the glass surface increases so much that the preferential adsorption of carbon disulphide begins, the long-range and short-range forces compete with one another, promoting the disposition of different phases near the substrate and there is no wetting.

With increase in long-range forces, new effects appear on the phase diagrams:[92] a sequence of wetting transitions arises near T_c and wetting layers with different concentration profiles are observed in different temperature ranges. The parameter g^* plays a significant role under these conditions.

An important problem in the experimental investigation of wetting transitions is the quality of the substrate surface. In the theoretical study of this question, the wall is assumed to be ideally smooth, so that the interactions between the substrate and the liquid molecule depend solely on the coordination at right angles to the surface. However, the imperfection of the surface or the presence of impurities, both in the material itself and adsorbed on the latter, lead to random variations in the energy of the interaction of the molecules with the substrate in the plane of its surface. A recent analysis of experimental data has shown[106] that the inconstancy of the wetting energy (even when the best of the available substrates are used) influences significantly the adsorption isotherm near the two-dimensional liquid–vapour critical point. The study of this process in relation to wetting transitions[107,108] has shown that the random energy inhomogeneity of the wall does not affect the critical wetting transition and promotes a continuous variation of the degree of adsorption when the system passes from the weak adsorption region to the strong adsorption region (on intersection of the *PW* line on the phase diagrams).

VII. FLUCTUATIONS IN THE WETTING LAYERS AND CRITICAL PARAMETERS OF WETTING TRANSITIONS

In considering the wetting phenomena, we neglected previously the fluctuations in the wetting film. The underestimation of the role of fluctuations in describing the PT in the bulk phase makes the results obtained using classical theories inaccurate in the vicinity of T_c.[1–3,5] Only for systems where there are strong interactions between the molecules over long distances and for polymer blends[109–111] (with the exception of a narrow temperature range near T_c) are the conclusions based on the average field theory reliable. Appreciable interest has arisen recently in the study of fluctuations in wetting layers[30,74,87,88,97–100,112,129] and in the elucidation of their influence on the stability of the layer. Attention has been concentrated on the study of capillary waves arising at the boundaries of the wetting layer. At the same time, the appearance of fluctuations of another kind, capable of preventing the formation of a wetting layer of

the denser phase at the boundary with the vapour, has also been noted.[39,112]

Below we shall consider briefly the fluctuations in the wetting films formed when a gas is adsorbed on a substrate. The presence of the film limits the fluctuations at the film–vapour boundary, but, under the conditions of the continuous increase in the thickness of the film (for critical wetting or for an increase in concentration up to saturation), the influence of the substrate weakens and the adsorption layer terminates as the almost free liquid-vapour interface. Many characteristics of the wetting transitions, including the critical phenomena, can be explained within the framework of the model of the layer with effective interactions between the surfaces bounding the film.[97–100,113–122] In this model, the surface fluctuations are described as the deviations $\delta(x, y)$ of the position of the free boundary of the film, corresponding to its local thickness $l(x, y)$, from the equilibrium thickness $\hat{l}$: $l(x, y) = \hat{l} + \delta(x, y)$, where x and y are coordinates in a plane parallel to the substrate surface. The functional of the free energy of the film assumes the form[113–118]

$$F[l] = \int dx\,dy\left[\frac{1}{2}\sigma_{\alpha\beta}(\nabla l)^2 + V(l)\right] = F[\hat{l}] + \\ + \int dx\,dy\left[\frac{1}{2}\sigma_{\alpha\beta}(\nabla\delta)^2 + \frac{1}{2}\left(\frac{\partial^2 V(l)}{\partial l^2}\right)_{\hat{l}}\delta^2 + O(\delta^3)\right].$$

The first term describes the change in free energy as a result of the increase in the surface area as a result of the fluctations in $l(x, y)$: $V(l)$ is the effective potential of the film (it determines whether or not the attraction or repulsion of the free surface of the film by the well depends on the potentials of the interactions of the molecules with the substrate). If the attraction between the surfaces bounding the film is fairly strong and retains the free film surface at a certain distance l from the wall, then the change in conditions is accompanied by a continuous decrease in this attraction. We shall assume that the substrate is impermeable to the molecules of the liquid. Then the potential $V(l)$ of the wetting films formed from the single-phase systems depends on the extent to which the vapour has failed to reach saturation and in the case of surface forces with small radius of action has the following form:[115–119,123]

$$V(l) = A\exp(-\tau l) + |\Delta\mu|\,l, \tag{30}$$

while in the case of long-range forces we have[115–118]

$$V(l) = Bl^{-m} + |\Delta\mu|\,l, \tag{31}$$

where A, B, and τ are coefficients and $\Delta\mu$ is the deviation of the chemical potential from its value on the coexistence curve. Wetting in model systems whose potential $V(l)$ is described by Eqns.(30) and (31) takes place for positive values of the coefficients A and B, whereupon $\Delta\mu \to 0$.

In the model considered, the dependence of the equilibrium film thickness $\hat{l}$, the correlation radius of the surface fluctuations $\xi_{\|}$, and the interfacial free energy on the degree of unsaturation can be found from the relations

$$\left.\frac{\partial V(l)}{\partial l}\right|_{\hat{l}} = 0;\quad \sigma_{\alpha\beta}(\xi_{\|})^{-2} = \frac{\partial^2 V(l)}{\partial l^2};$$
$$\sigma_s = V(\hat{l}). \tag{32}$$

The character of the variation of these quantities for $\Delta\mu \to 0$ makes it possible to determine the critical parameters of the wetting transition β_s, $\nu_{\|}$, and α_s:

$$\hat{l} \propto |\Delta\mu|^{\beta_s};\quad \xi_{\|} \propto |\Delta\mu|^{-\nu_{\|}};\quad \sigma_s \propto |\Delta\mu|^{2-\alpha_s} \tag{33}$$

For systems where only small-radius interaction forces exist, it follows from Eqns.(30), (32), and (33) that $\beta_s = 0$, $\nu_{\|} = 1/2$, and $\alpha_s = 1$; if the intensity of the interactions between the liquid molecules and the substrate diminishes in accordance with a power law, the critical parameters depend on the parameter m in Eqn.(31):

$$\beta_s = -(m+1)^{-1};\quad \nu_{\|} = (m+2)/(2m+2),$$
$$\alpha_s = (m+2)/(m+1)$$

[for non-lagging van der Waals forces ($m = 2$), we have $\beta_s = -1/3$, $\nu_{\|} = 2/3$, and $\alpha_s = 4/3$ [114–118,123]]. Thus the appearance of a macroscopic wetting layer on the substrate surface as the coexistence curve is approached is accompanied by an increase in fluctuations on the free surface of the layer. This factor indicates the similarity of the behaviour of the systems in the wetting transitions to the behaviour of the bulk-phase systems near the critical point.

The question arises whether the growing fluctuations alter the results obtained within the framework of the average field theory for surface wetting transitions. An answer may be obtained by estimating with the aid of a suitable hyperscaling relation,[116,118] for example:

$$(d-1)\nu_{\|} = 2 - \alpha_s \tag{34}$$

the limiting number of dimensions d^* of the space.[1–3] The character of the variation of the quantities $\hat{l}$, $\xi_{\|}$, and σ_s as a function of $\Delta\mu$ is predicted correctly by the average field theory, provided that the number of dimensions of the space in which the transition is investigated is greater than d^*. By substituting in Eqn.(34) the values of $\nu_{\|}$ and α_s quoted above, it is possible to find d^*. For the modelling of the interactions in the film by means of the potential defined by Eqn.(30), we have $\nu_{\|} = 1/2$ and $\alpha_s = 1$, so that $d^* = 3$. Additional analysis of this case showed[117] that, for a three-dimensional space, the average field theory yields the correct values of the wetting parameters. Under the conditions of long-range action, the quantity d^* is extremely sensitive to the character of the variation of the forces: $d^*(m) = (3m + 2)/(m + 2)$, but, for finite values of m, the quantity $d^*(m) < 3$ (long-range forces diminish d^*, as for the critical phenomena in the bulk phase). Thus the average field theory describes correctly the influence of the substrate surface on total wetting transitions.

Critical wetting is also accompanied by an increase in surface fluctuations. The parameter $\nu_{\|}$ in the temperature variation of the correlation radius, calculated in accordance with the average field theory for models in which the existence of only forces with a small radius of action is postulated, is 1, while $d^* = 3$.[116,124] However, in critical wetting the role of fluctuations is more significant; $\nu_{\|}$ loses its universality and depends on the dimensionless parameter $\omega = k_B T(4\pi\sigma_{\alpha\beta}\xi_{\|}^2)^{-1}$. Three ranges of ω values have been differentiated:[119–122,125] $\omega < 1/2$ with $\nu_{\|} = (1 - \omega)^{-1}$, $1/2 < \omega < 2$ with $\nu_{\|} = (2^{1/2} - \omega^{1/2})^{-2}$, and $\omega > 2$ with $\nu_{\|} = \infty$. It has been suggested[122,128] that, for pure liquids, their binary mixtures, and polymer systems (as well as other systems which belong to this class of universality), the parameters ω near T_c refer to the second region (according to Moldover,[13] $\omega \simeq 0.8$). If the fluctuations in the wetting films are small, then $\nu_{\|} = 1$. The transition from the classical forms of critical conditions, obtained on the basis of the average field theory, to the non-classical form occurs when the correlation radius of the surface fluctuations is equal to to 5–6 molecular diameters.[129] The experimental confirmation of the relations described in real systems, where long-range forces play an important role, is hardly feasible.

Under the conditions of the existence of long-range forces, the critical behaviour of three-dimensional systems is independent of the surface tension and surface fluctuations do not alter the average field

regime.[99,119] For potentials of the type $V(l) = A(T - T_{cW})l^{-n} + Bl^{-m}(A, B > 0, m > n > 0)$, we have $\beta_s = -1/(m-n)$ and $\nu_{||} = (m+2)/2(m-n)$. So far the problem of the experimental confirmation of the theory remains open.

VIII. CRITICAL ADSORPTION

The picture of the influence of the surface on PT in two-component systems must be supplemented by considering the adsorption of the components from a homogeneous mixture having the critical composition. It has been established that in the vicinity of T_c an anomalous increase in the degree of adsorption of one of the mixture components on the surface of the wall is observed. This phenomenon is called critical adsorption. Its essential feature reduces to the following. Under the conditions of the preferential interaction of one of the components with the wall, the composition of a mixture of liquids changes over distances from the wall surface comparable to the correlation radius of the fluctuations in the bulk phase. Since the approach to T_c induces a sharp increase in the fluctuations in the system, within a certain concentration and temperature range near the critical point, an extended region should arise at the substrate surface in which the mixture composition differs from the bulk-phase composition. The closer the system is to the critical point, the wider the layer of liquid in which the composition is modified.

The critical adsorption phenomenon, first observed by Rusanov and co-workers,[130-132] has become the subject of intense theoretical and experimental studies. It is possible to distinguish two theoretical approaches to the consideration of critical adsorption in two-component systems. The first of these is based on the thermodynamic Gibbs relation for adsorption:[133]

$$\Gamma_{B(A)} = -\left(\frac{\partial\sigma}{\partial\mu}\right)_T = -\left(\frac{\partial\sigma}{\partial\varphi}\right)_T\left(\frac{\partial\varphi}{\partial\mu}\right)_T, \tag{35}$$

(where $\Gamma_{B(A)}$ is the relative degree of adsorption) and requires knowledge of the equation of state and of the character of the variation of the surface tension as a function of mixture composition and temperature in the critical region. In modern theories of critical phenomena,[1-3] the dependence of the chemical potential on composition is described by the expression $|\mu - \mu_c| \simeq |\varphi - \varphi_c|^{4.8}$, where μ_c is the critical potential of component B in the mixture at the critical point. The studies by Widom and co-workers[134-138] have led to the conclusion that, in the vicinity of the critical point, the surface tension is a monotonic function of composition, increasing with increase in the concentration of the component with a higher value of σ. At the critical temperature, the form of the function $\sigma(\varphi)$ is analogous to the form of the critical isotherm for a one-component liquid. The form of the dependence of the surface tension on concentration has been established:[133,138]

$$|\sigma - \sigma_c| \propto |\varphi - \varphi_c|^{\mu/\beta}, \mu/\beta \cong 3.9. \tag{36}$$

When the classical values of the critical parameters $\mu = 3/2$ and $\beta = 1/2$ are used, the concentration dependence of the deviation of the surface tension from its value at the critical point σ_c becomes more pronounced:[133,134]

$$|\sigma - \sigma_c| \propto |\varphi - \varphi_c|^3 \ln[|\varphi - \varphi_c|^{-1}]. \tag{37}$$

The experimental data for the nitrobenzene–hexane,[131] nitroethane–3-methylpentane,[137] and isobutytric acid–water[137,138] systems agree with the principal theoretical conclusions concerning the character of the variation of σ with concentration. However, the inadequate accuracy of the methods for the measurement of surface tension and the methodological difficulties arising in measurements in the critical region makes it impossible to determine which of the relations (36) and (37) holds.

The temperature dependence of the degree of adsorption near T_c can be obtained from Eqns.(35)–(37):

$$\Gamma_{B(A)} \propto |t|^{\beta-\nu} = |t|^{-0.3}, \tag{38}$$

$$\Gamma_{B(A)} \propto \ln|t^{-1}|, \tag{39}$$

where ν is the critical exponent in the temperature variation of the correlation ranges of the volume fluctuations. (The classical form of the equation of state $|\mu - \mu_c| \propto |\varphi - \varphi_c|^3$ is used in the derivation of the last relation.)

The second way of investigating critical adsorption is associated with the elucidation of the concentration profile at the interface beween the binary liquids with the critical composition and the wall. This procedure can be used in the analysis of the liquid–vapour and liquid–solid interfaces. A wide variety of theoretical approaches are adopted for the investigation of the form of the concentration profile: the average field theory,[134-136] scaling,[139] the renormalised group method,[140-142] and the method of functional expansions.[143-145] We may note that in the case under consideration an approximation is used according to which the existence of surface forces with a small radius of action is postulated. This approximation is entirely justified, since, with increase in the correlation radius, the wall has no influence over long distances ($z > \xi$).

The average field theory postulates a slow decrease in the concentration of the adsorbed component with increase in the distance from the surface:[133,134,143]

$$\Delta\varphi(z) = \varphi(z) - \varphi_c \propto z^{-1}. \tag{40}$$

More realistic models, constructed either on the basis of the equations of state for two-component liquids, reflecting the real features of the critical systems,[133,135,140,143,144] or using modern theories of critical phenomena,[139-142] yield a different form of the concentration profile. According to a number of workers,[139-142] one of the mixture components is adsorbed preferentially at the boundary with the substrate at the critical point, the decrease in the concentration of this component on moving away from the wall obeying the law

$$\Delta\varphi(z) \propto z^{-\beta/\nu}. \tag{41}$$

If the experimental temperature differs from T_c, then Eqn.(41) holds only within the limits of the correlation radius and is then replaced by another equation according to which the composition changes faster:

$$\Delta\varphi(z) \propto \exp(-z/\xi), \quad z \gg \xi. \tag{42}$$

The excess concentration of the adsorbed component can be determined by analysing the profile

$$\Gamma \propto \int_0^\infty \Delta\varphi(z)\,dz. \tag{43}$$

In order to elucidate the character of the temperature variation of the degree of adsorption, one introduces the hypothesis that, over distances exceeding the molecular size a, Eqns.(41) and (42) hold, while in the range $0 < z < a$ the concentration is constant and $\varphi(z) = \varphi_s$. In this case, the surface excess is described by an expression of the type

$$\Gamma = a\varphi_s\left[\frac{2\nu-\beta}{\nu-\beta}\left(\frac{\xi}{a}\right)^{1-\beta/\nu} - \frac{\beta}{\nu-\beta}\right] \propto |t|^{\beta-\nu}. \tag{44}$$

(For a liquid–vapour interface, a similar discussion has been published elsewhere.[133-136,143-145])

The critical liquid–vapour[130–132,146–150] and critical liquid–solid wall[151–155] interfaces are studied experimentally with the aid of a wide variety of optical methods. In the studies quoted above, an anomalous behaviour of structure-centred parameters in the vicinity of the critical point has been noted. In the study of the surface of the nitrobenzene–hexane binary mixture having a nearly critical composition, a sharp increase in the ellipticity coefficient was observed in the vicinity of T_c.[130,142] Ellipsometric studies of the liquid–vapour interfaces in various critical mixtures have been continued.[150] Rusanov and Pshenitsyn,[130] Peliti and Leibler,[142] and Schmidt and Moldover[150] concluded that the observed anomalies are caused solely by surface phenomena and indicate an increase in the degree of adsorption in the critical region. Critical adsorption of the components of the nitrobenzene–hexane mixture on a glass surface has been investigated by the fluorescence method.[151] The increase in the fluorescence intensity near the critical point is explained by the selective interaction of nitrobenzene with glass. It has been established[152–154] that an increase in the intensity of the reflection of light from the interface between glass and a mixture of nitromethane with carbon disulphide is due to the critical adsorption of nitromethane; the change in the polarity of the glass induced by making it hydrophobic promoted the preferential interaction of carbon disulphide with the substrate and the consequent decrease in the reflection coefficient.

Although there is convincing evidence for the anomalously high degree of adsorption in the critical region, a quantitative interpretation of the experimental results presents certain difficulties. Firstly, it is necessary to establish the relation between the parameters measured experimentally and the degree of adsorption[146,149] and the distribution of concentration in space.[76,148,150,155] Secondly the conclusion about the temperature variation of the degree of adsorption or about the concentration profile must be based on a comparison of relations fairly similar in form: $\Gamma \propto \ln(t^{-1})$ and $\Gamma \propto (t)^{-0.3}$, $\Delta\varphi(z) \propto z^{-1}$ and $\Delta\varphi(z) \propto z^{-1/2}$. These factors are apparently the cause of the ambiguous interpretation of the experimental data. Thus a logarithmic temperature dependence of the degree of adsorption of cyclohexane at the interface with vapour from solutions in aniline has been established.[146,147] It has been found[149] that the critical adsorption parameter is 0.35 ± 0.15, but at the same time there is a temperature range in which the results are described satisfactorily by linear relation between Γ and $\ln(t^{-1})$. On the basis of a study of the temperature variation of the ellipticity coefficient of the light reflected from the interface between the vapour and a solution of polystyrene in cyclohexane, it has been demonstrated[75] that, for the critical adsorption of the solvent, the concentration profile corresponds to Eqns.(41) and (42). The data of Heidel and Findenegg[148] also agree with the model for which Eqns.(41) and (42) are valid, but the $\Delta\varphi(z) \propto z^{-1}$ relation cannot be fully excluded. The application of the methods for the solution of the converse ellipsometric problem developed recently may prove useful for the final elucidation of the question of the distribution of concentration in the adsorption layer under the conditions of critical adsorption, together with an increase in experimental accuracy.[156]

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It follows from the data presented that the presence of the wall leads to the appearance of a whole range of transitions near the surface. The study of the physics of phase transitions and of the physical chemistry of surfaces has ensured during the last 5–10 years rapid progress in the theory of transitions induced by the presence of the wall. In a brief review, it is impossible to reflect fully all the fine details of the models used in the consideration of various aspects of wetting transitions and to discuss comprehensively all the theoretical results obtained with their aid. Preference has been given to the clearest data reflecting important aspects of the phenomenon.

The experimental study of the problem requires considerable effort associated both with the preparation of the objects of study and with the careful thermostatic control of the system, on the one hand, and with the long equilibration time, on the other. So far there are no experimental data on wetting transitions in polymer systems, although certain hopes for the attainment of a combination of the interactions between the components which is manifested in the form of critical wetting are in fact associated with precisely these systems. There are scanty data concerning the existence in a homogeneous system of regions characterised by significantly different degrees of adsorption of the mixture components on the substrate. There have been no studies whatever of labile states of the surface layer. These and other questions require comprehensive consideration.

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Oxidation of Sulphur Dioxide in Aqueous Solutions

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The sulphur dioxide oxidation reactions in aqueous solutions under mild conditions are examined. The kinetics of the oxidation of SO_2 to H_2SO_4 by various oxidants are described, the reaction mechanism is discussed, and its possible practical applications are indicated.
The bibliography includes 96 references.

CONTENTS

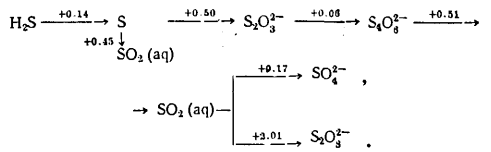
I. Introduction 1029
II. Catalytic and non-catalytic reactions involving the oxidation of SO_2 by various compounds 1030
III. Catalytic reactions involving the oxidation of SO_2 by molecular oxygen 1035
IV. Conclusion 1037

I. INTRODUCTION

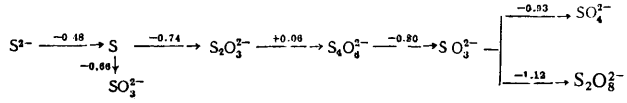
The SO_2 oxidation reactions under mild conditions are of interest from the theoretical point of view for the study of the detailed mechanism of the inner-sphere transformations of the substrate molecules. The study of such processes is important also from the practical point of view because they can be used to develop methods for the elimination of the highly toxic component (sulphur dioxide) from the waste gases generated in metallurgical and other industries. (The discharged sulphur dioxide is known to cause considerable damage in nature, to spoil buildings and equipment, and to cause their breakdown.) Although the SO_2 concentration in waste gases is usually low, its overall release throughout the world can be measured in hundreds of millions of tonnes. Therefore, together with the solution of the ecological problems, the utilisation of waste gases makes it also possible to obtain large amounts of sulphuric acid. The use of liquid-phase catalysts is desirable precisely in the oxidation of gas mixtures with a low SO_2 content where heterogeneous catalysts are ineffective.

Three types of reactions are characteristic of sulphur dioxide: reactions occurring without change (a), with decrease (b), and with increase (c) in the valence of sulphur. The oxidation state of sulphur in compounds varies from -2 to +6. In the schemes below, the oxidation-reduction potentials of the corresponding transitions between different sulphur compounds are indicated above the arrows (in V):[1]

(1) Acid solutions:



(2) Alkaline solutions:



The dissolution of SO_2 in water with formation of hydrates and sulphurous acid may serve as an example of reactions in which there is no change in the valence of sulphur:

$$H_2O + SO_2 \rightleftharpoons H_2SO_3 \overset{K_1}{\rightleftharpoons} H^+ + HSO_3^- \overset{K_2}{\rightleftharpoons} 2H^+ + SO_3^{2-}, \qquad (1)$$

where $pK_1 = 1.92$ and $pK_2 = 7.2$.[1] The interaction of sulphur dioxide with bases and the salts of weak acids leads to salts of sulphurous acid.[2]

There is no direct proportionality between the total absorption of SO_2 and its partial pressure (above 1 atm), i.e. Henry's law is not applicable to the dissolution of SO_2 in water.[2] On the other hand, it has been established that the dependence of the solubility of SO_2 in water on pressure (up to 1 atm) is close to linearity. The solubility of SO_2 in sulphuric acid at pressures up to 1 atm obeys Henry's law. With increase in the H_2SO_4 concentration from 0 to 85%, the solubility of SO_2 gradually falls, while in more concentrated acid solutions it increases.[3]

The dissolution of SO_2 in water and sulphuric acid is widely used in chemical industry. The dependence of the solubility of sulphur dioxide on its partial pressure and also on temperature and acidity has been studied in detail,[3] which is important for the solution of practical problems in the manufacture of sulphuric acid. According to equilibrium (1), the solubility of SO_2 in water can be increased by lowering the H^+ concentration or by removing sulphite ions by oxidising them to sulphate ions. However, in the latter case the concentration of H^+ ions increases somewhat, since the H_2SO_4 formed is more ionised than sulphurous acid: this partly weakens the influence of the decrease in the sulphite concentration on the solubility of SO_2.[4]

The physicochemical principles of the sulphur dioxide extraction and concentration processes have been examined in greatest detail by Rozenknop,[2] who quotes the solubilities of SO_2 in water, in solutions of strong acids and bases as well as salts, and in heterogeneous systems and provides equations from which it is possible to calculate the temperature dependence of the vapour pressures of sulphur dioxide solutions.

The heats of the reactions occurring during the absorption of SO_2 have the following values:[2]

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 + 26 \text{ kJ},$$
$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- + 16 \text{ kJ}.$$

If the absorber is a base, then

$$H^+ + OH^- \rightleftharpoons H_2O + 56 \text{ kJ}.$$

If the absorber is the salt of a weak acid, then the heat of absorption of SO_2 is equal to the heat of ionisation of this acid.

The most suitable absorbers for sulphur dioxide are the following buffer solutions at fairly high pH:[5] (1) solutions of salts of a weak acid and a strong base (for example, sodium sulphite and bisulphite); (2) solutions of salts of a strong acid and a weak base (for example, basic aluminium sulphite); (3) solutions of salts of a weak acid and a weak base (for example, ammonium sulphite and bisulphite); (4) solutions of salts of weak acids in the presence of the free acid (sulphites and bisulphites in the presence of organic acids). Water is used to absorb SO_2 from gases when its concentration is $\geqslant 7$ vol.%; for more dilute gases, this method is uneconomical because of the large consumption of water and the expenditure of heat on desorption.[5]

The kinetics of the absorption of sulphur dioxide by solutions of ammonia and ammonium sulphite-bisulphite have been investigated[6] at 298 K and it has been established that, when SO_2 is absorbed by NH_3 solutions, the following rapid two-stage reaction takes place:

$$SO_2 + 2NH_3 \xrightarrow{H_2O} (NH_4)_2 SO_3,$$

while in solutions of ammonium sulphite an irreversible interaction of SO_2 with SO_3^{2-} ions occurs. The study of the kinetics of the absorption of sulphur dioxide by NH_4OH, NaOH, KOH, Na_2CO_3, and Na_2SO_3 solutions showed[7] that, with decrease in their concentration, the rate of absorption of SO_2 increases for all the absorbers except sodium sulphite. In this case the chemisorption process is limited by the diffusion of SO_2 in the liquid phase and the viscosity of these solutions increases linearly with their concentration. The order of the reaction with respect to SO_2 is close to zero.

The absorbers can be arranged in the following sequence in terms of decreasing SO_2 absorption rate constants (at 293 K):

$$NH_4OH\ (8.99) > KOH\ (5.126) > NaOH\ (5.078) > Na_2CO_3\ (4.931) > > Na_2SO_3\ (4.217\ m^3\ kmol^{-1}\ h^{-1}).$$

The equation for the rate of reaction for different compounds can be written in the general form

$$w = Ae^{-B\tau},$$

where τ is the time in min and A and B are constants which depend on the nature of the absorber and have the following values: 5.8521 and 0.0469 for Na_2SO_3; 6.314 and 0.0254 for Na_2CO_3; 6.6205 and 0.0173 for KOH; 7.3205 and 0.0151 for NaOH; 9.9144 and 0.0048 for NH_4OH.

Few chemical processes are accompanied by a decrease in the valence of sulphur. The reactions of SO_2 with hydrogen sulphide and carbon monoxide may serve as examples:[2]

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S,$$
$$SO_2 + CO \rightarrow 2CO_2 + S.$$

Reactions occurring with increase in the valence of sulphur are most characteristic of sulphur dioxide. Thus sulphur dioxide combines with chlorine even in sunlight. The interaction of SO_2 with oxygen proceeds as a rule at a high temperature and in the presence of catalysts:[2]

$$2SO_2 + O_2 \xrightarrow{\text{catalyst}} 2SO_3.$$

In an aqueous medium, the oxidation of sulphur dioxide by compounds (ions) with a high oxidation-reduction potential is fairly rapid. In most cases, the process then proceeds with formation of sulphuric acid via a mechanism which we believe to involve the oxidative sulphonation of water[8] and subsequent regeneration of the reduced species Red by molecular oxygen:

$$SO_2 + 2H_2O + Ox \rightarrow H_2SO_4 + Red + 2H^+,$$
$$Red + O_2 + 4H^+ \rightarrow Ox + 2H_2O,$$
$$SO_2 + O_2 + 2H^+ \rightarrow H_2SO_4.$$

The oxidation of SO_2 in aqueous solutions to sulphuric acid is very important for the extraction of sulphur dioxide from gases, but it has still been inadequately investigated.[9]

Numerous studies have been devoted to the high-temperature heterogeneous processes involving the oxidation of SO_2 to SO_3—the main method of synthesis of sulphuric acid.[10–15] On the other hand, the oxidation of SO_2 under mild conditions has been described in the literature to a much lesser extent, although it is attractive from the standpoint of economising on energy resources and leads to new possibilities for the investigation of the mechanism of catalysis by complex compounds and solutions.

II. CATALYTIC AND NON-CATALYTIC REACTIONS INVOLVING THE OXIDATION OF SO_2 BY VARIOUS COMPOUNDS

In aqueous media, the oxidation of sulphur dioxide by complex metal anions and molecular oxygen under the influence of homogeneous catalysts is fairly rapid with the formation of H_2SO_4. Table 1 indicates the metal ions (M^{n+}) which oxidise SO_2 to H_2SO_4 in aqueous solutions and also the energetic and kinetic characteristics of oxidation-reduction reactions of the type:

$$2M^n + SO_2 + 2H_2O \rightarrow 2M^{n-1} + H_2SO_4 + 2H^+.$$

Table 1. Kinetic and energetic characteristics of the processes leading to the oxidation of SO_2 to H_2SO_4 in aqueous solutions.

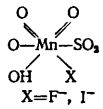
Ion	Active form of complex ion	T, K	Rate constant	E_a, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}	Refs.
Mn^{7+}	$MnO_3(OH)I^-$ (aq)	293	1.15×10^6 litre mol^{-1} min^{-1}	7.2	—178	[16]
Mn^{7+}	$MnO_3(OH)F^-$ (aq)	293	75.7×10^3 litre mol^{-1} min^{-1}	38.0	—92	[16]
Cr^{6+}	$CrO_3(OH)^-$ (aq)	298	18.0×10^4 litre mol^{-1} min^{-1}	—	—	[17, 18]
Cr^{6+}	$CrO_3(OH)I^{2-}$ (aq)	298—318	2.0×10^5 litre mol^{-1} min^{-1}	5.6	—	[17, 18]
Se^{4+}	$SeO_m(OH)_n I^{3-2m-n}$(aq)	293—323	7.2×10^4 litre^2 mol^{-1} min^{-1}	13.4	—	[18]
Hg^{2+}	HgX_n^{2-n}(Ac$^-$, NO_3^-)	303	0.5×10^2 litre^2 mol^{-2} min^{-1}	—	—	[19]
Fe^{3+}	$Fe(CN)_6^{3-}$ (aq)	298	0.52 litre^2 mol^{-2} min^{-1}	—	—	[20]
Cu^{2+}	$CuCl_2I^-$ (aq)	293—343	3.9×10^2 litre^2 mol^{-2} min^{-1}	32.6	—104.6	[21]
Cu^{2+}–Fe^{3+}	$CuFeCl_nI^{4-n}$ (aq)	293—353	3.6×10^3 litre^2 mol^{-2} min^{-1}	30.0	147.6	[22, 23]

Notation. T is the temperature, E_a the activation energy, and ΔS^* the activation entropy.

The oxidation of sulphur dioxide by manganese(VII), chromium(VI), and selenium(IV) compounds and $S_2O_8^{2-}$ has been studied in detail.[16–18,24,25] Thus potassium permanganate is readily reduced by sulphur dioxide in the presence of the F^-, I^-, or OH^- ions in accordance with the stoichiometric equation[16]

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+.$$

The reaction is of first order with respect to the oxidant, the reductant, and H^+ ions. It is believed that the rate-limiting stage of the process is inner-sphere redox decomposition of the intermediate complex incorporating all the reaction components:



Depending on the nature of the ligand-catalyst (OH^-, F^-, I^-), which effects electron transfer between the oxidant and the reductant, the rate of the process varies significantly: the activity of the ligands increases in the sequence $F^- < OH^- < I^-$. It is believed that the high activity of the I^- ion is due to the fact that it is a stronger nucleophile than the F^- and OH^- ions.[16]

Sulphur dioxide is oxidised by chromium(VI) in accordance with the equation

$$2CrO_4^{2-} + 3SO_2 + 4H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 2H_2O.$$

In the range of $HClO_4$ concentrations up to 10 M, the reaction is of first order with respect to Cr^{3+}, SO_2, and H_3O^+.[17,18] The proposed reaction mechanism includes the formation of the protonated form of chromium(VI) with subsequent addition to the latter of a SO_2 molecule. The stage in which the chromium(VI) complex of sulphur dioxide $CrO_3(OH)SO_2^-$(aq.) decomposes is rate-limiting:

$$\begin{gathered} SO_2 \overset{H_2O}{\rightleftharpoons} SO_2\,(aq), \\ CrO_4^{2-} + H_3O^+ \rightleftharpoons CrO_3\,(OH)^-\,(aq) + H_2O, \\ CrO_3\,(OH)^-\,(aq) + SO_2 \rightleftharpoons CrO_3\,(OH)\,SO_2^-\,(aq) + H_2O, \\ CrO_3\,(OH)\,SO_2^-\,(aq) \rightarrow CrO_3^- + HSO_3, \\ 2HSO_3 \rightarrow H_2SO_4 + SO_2. \end{gathered}$$

The rate of reaction is described by the equation

$$w = k \cdot [CrO_3\,(OH)\,SO_2^-\,(aq)].$$

The oxidation of sulphur dioxide by selenous acid[18]

$$H_2SeO_3 + 2SO_2 + H_2O \rightarrow Se + 2H_2SO_4$$

is greatly accelerated in the presence of proton-ligand catalysts. In the $H_2SeO_3 - HClO_4 - KI - H_2O$ system, the reaction is of first order with respect to Se^{4+}, SO_2, and KI; the order with respect to hydrogen ions is close to two. According to the reaction mechanism proposed,[18] hydrogen ions protonate the oxygen atoms in the SeO_3^{2-} anion after which the protonated forms form complexes with the dissolved sulphur dioxide and I^- ions:

$$\begin{gathered} SeO_3^{2-}\,(aq) + j\,H_3O^+ \rightleftharpoons SeO_m\,(OH)_n^{4-2m-n}\,(aq) + j\,H_2O, \\ SeO_m\,(OH)_n^{4-2m-n}\,(aq) + I^- \rightleftharpoons SeO_m\,I^{3-2m-n}\,(OH)_n\,(aq), \\ SeO_m I\,(OH)_n^{3-2m-n}\,(aq) + SO_2\,(aq) \rightleftharpoons SeO_m\,(OH)_n\,I\,(SO_2)^{3-2m-n}\,(aq). \end{gathered}$$

The redox reaction of the complexes $SeO_m(OH)_nISO_2^{3-2m-n}$(aq.) in stage (2) limits the rate of the process. The subsequent reduction of selenium(III) is rapid and is not reflected in the reaction kinetics:

$$\begin{gathered} SeO_m\,(OH)_n\,I\,(SO_2)^{3-2m-n}\,(aq) \rightarrow SeO_m\,(OH)_n\,(I^0)\,SO_2^{3-2m-n}\,(aq), \\ SeO_m\,(OH)_n\,(I^0)\,SO_2^{3-2m-n}\,(aq) \rightarrow Se^{3+} + I^- + HSO_3, \\ Se^{3+} + HSO_3 \rightarrow H_2SO_4 + Se^0. \end{gathered} \qquad (2)$$

The rate of reaction depends on the relative contents of the protonated forms $Se(IV) - SeO^{2+}$(aq.) and $SeOH^{3+}$(aq.) (κ_1 and κ_2 respectively) which exhibit the highest activity in the oxidation of sulphur dioxide:

$$w = (k_1\kappa_1 + k_2\kappa_2)\,[I^-]\,[SO_2],$$

where k_1 and k_2 are the partial rate constants.

It has been observed that sulphur dioxide is rapidly oxidised by mercury(II) to sulphuric acid in the presence of $HClO_4$ (at a concentration of 2–8 M) with formation of metallic mercury.[19] The reaction orders with respect to Hg^{2+} and SO_2 are close to unity. According to Golodov and Panov,[19] the process includes the following stages:

$$\begin{gathered} HgX_n^{2-n}\,(aq) + SO_2\,(aq) \rightleftharpoons HgX_nSO_3^{2-n}\,(aq) + H_2O, \\ HgX_nSO_3^{2-n}\,(aq) \xrightarrow{2H_2O} Hg^0 + SO_4^{2-} + 4H^+ + n\,X, \\ X^- = Ac^-,\ NO_3^-. \end{gathered}$$

The oxidation of SO_2 by hydrogen peroxide in aqueous solution (ionic strength 1.0; pH 4–8) is of interest.[26,27] For example, it has been established that the reaction orders with respect to SO_2 and H_2O_2 are unity and that with respect to hydrogen ions varies from 1 in the pH range 4.5–6.5 to 2 in the pH range 6.5–8.0. The reaction is accelerated in the presence of proton donors (HA) in conformity with the mechanism of general acid catalysis. It is believed that the process mechanism includes the following stages:

$$\begin{gathered} HSO_3^- \overset{K}{\rightleftharpoons} SO_3^{2-} + H^+, \\ HSO_3^- + H_2O_2 \rightleftharpoons H_2O + HOOSO^-, \\ HOOSO^- + HA \rightarrow H_2SO_4 + A^- \end{gathered}$$

($HOOSO^-$ is the monopersulphurous acid anion).

The rate of reaction is described by the equation

$$w = [H_2O_2]\,[SO_2]\,\{[H^+]/([H^+] + K)\}\,(k_1[H^+] + k_2[HA]),$$

where $k_1 = 58$ and $k_2 = 720$ litre^2 mol^{-2} s^{-1} at $T = 285$ K. The activation energy of the process is 37 ± 2 kJ mol^{-1} and the activation entropy is ~4 J mol^{-1} K^{-1}.

The oxidation of sulphur dioxide by sodium persulphate in the absence of catalysts,

$$Na_2S_2O_8 + SO_2 + 2H_2O \rightarrow Na_2SO_4 + 2H_2SO_4,$$

proceeds at low rates.[24,25] The reaction takes place vigorously when acted upon jointly by protic and ligand catalysts. It is believed that sulphur dioxide reacts in the form of HSO_3^- anions in the $Na_2S_2O_8 - HClO_4 - KI - SO_2 - H_2O$ and $Na_2S_2O_8 - HClO_4 - LiBr - SO_2 - H_2O$ systems, because it is known that the addition of the OH^- anion to SO_2 intensifies the reducing properties of the latter as a result of the increase in electron density in the donor orbital of the S atom.[28]

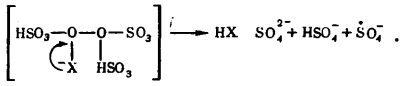
It has been suggested[28] that HSO_3^- anions are oxidised in the following way. The protonated form of the persulphate anion interacts initially with the halide ion X^-, i.e.

$$S_2O_7OH^-\,(aq) + X^- \rightleftharpoons [S_2O_7\,(OH)\,X]^{2-}\,(aq),$$

and the complex $[S_2O_7(OH)X]^{2-}$(aq.) then reacts with HSO_3^-:

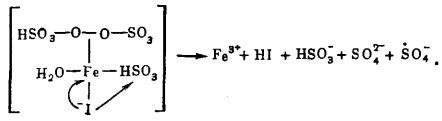
$$[S_2O_7\,(OH)\,X]^{2-}\,(aq) + HSO_3^- \rightleftharpoons [S_2O_7\,(OH)\,XHSO_3]^{3-}\,(aq).$$

In the rate-limiting stage, the active complex undergoes a redox reaction via the following mechanism:



It is believed[28] that the ligand (halide ion) gives up its electron to the peroxide linkage in the persulphate ion and then in the form X^0 oxidises HSO_3^-, being itself reconverted into X^-. Such electron redistribution takes place within the limits of the inner sphere of the complex.

The rate-limiting stage in the oxidation of HSO_3^- anions by persulphate anions in the presence of iron(III) is the reaction[25]



The iodide ion gives up its electron to the central atom of the complex, attacks the coordinated donor in the inner sphere, and is reduced to I. In its turn, Fe^{3+} transfers an electron to the peroxide linkage of the persulphate ion, as a result of which the latter is ruptured with subsequent decomposition of the complex. The reaction mechanism in the presence of iron(III) ions differs from that examined above in the fact that the metal in the complex facilitates the electron transfer from the iodide ion to the persulphate ion.

The oxidation of sulphite anions by the individual Fe^{3+} hexacyanoferrate(III) complex has also been investigated at 298 K.[20] The authors believe that the process proceeds as follows:

$$SO_3^{2-} + Fe(CN)_6^{3-} \rightleftharpoons Fe(CN)_6^{4-} + \dot{S}O_3^-,$$
$$Fe(CN)_6^{3-} + \dot{S}O_3^- \rightarrow Fe(CN)_5(CN\dot{S}O_3)^{4-},$$
$$Fe(CN)_5(CN\dot{S}O_3)^{4-} + H_2O \rightarrow Fe(CN)_6^{4-} + SO_4^{2-} + 2H^+.$$

The rate of reaction is described by the equation

$$\omega = k_M[M][SO_3^{2-}][Fe(CN)_6^{3-}],$$

where M is the Na^+ or K^+ ion, $k_{Na^+} = 0.52 \pm 0.02$ litre^2 mol^{-2} s^{-1}, and $k_{K^+} = 1.15 \pm 0.04$ litre^2 mol^{-2} s^{-1}. The oxidation of sulphite anions by hexacyanoferrate is weakly inhibited by molecular oxygen.

The liquid-phase oxidation of SO_2 by iron salts has been studied in acid solutions.[29] The increase in the $HClO_4$ concentration from 0.1 to 2.5 M leads to the formation in solution of the $SO_2.H_2O$ species, whose reactivity is low, as a result of which the rate of the process falls. The reaction orders with respect to SO_2 and Fe^{3+} are close to unity. The reaction mechanism presupposes the formation of the thionate radical HSO_3, which reacts with Fe^{3+} to form sulphate anions.

It has been observed[30] that Co^{3+} salts are more effective catalysts of the oxidation of sulphite ions than Fe^{3+} and Fe^{2+} salts. In the presence of cobalt nitrate, the concentration of sulphite ions at room temperature decreases by a factor of 7 in 3 h. A similar catalytic solution may be used to purify gases with a low SO_2 content.

The oxidation of sulphur dioxide by copper halides in the $CuCl_2-HCl-KI-H_2O$, $CuBr_2-HBr-KI-H_2O$, and $CuBr_2-LiBr-H_2O$ systems has been studied in greatest detail.[18,21,31] It takes place in accordance with the equation

$$2CuX_2 + SO_2 + 2H_2O \rightarrow 2CuX + H_2SO_4 + 2HX. \quad (3)$$

The reaction orders with respect to copper(II) and SO_2 were shown to be close to unity. Univalent copper increases the initial rate of the process by activating HSO_3^- anions (Figs.1 and 2).

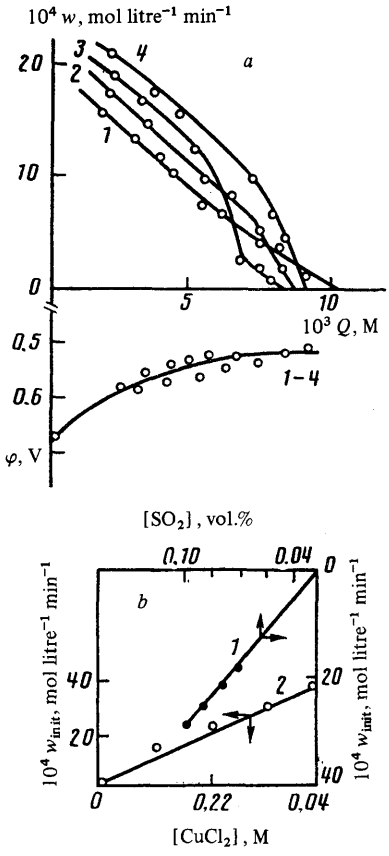


Figure 1. Oxidation of SO_2 by copper(II) chloride at 293 K, [HCl] = 4.8 M, and [KI] = 8 × 10^{-4} M: (a) dependence of the rate of oxidation w and of the potential of the system φ (calculated with respect to the hydrogen electrode potential) on the amount of SO_2 which has reacted for $[CuCl_2]$ = 0.02 M and different initial SO_2 concentrations (vol.%) [(1) 0.062; (2) 0.076; (3) 0.086; (4) 0.103]; (b) dependence of the initial rate of oxidation on $[SO_2]$ (line 1) for $[CuCl_2]$ = 0.02 M and on $[CuCl_2]$ (line 2) for $[SO_2]$ = 0.086 vol.%.[18]

The reduction of Cu^{2+} to Cu^+ takes place in the inner-sphere redox decomposition of Cu^{2+} complexes with HSO_3^- anions via two parallel pathways:

(a) first pathway (X^- = halide ion):

$$CuX_mHSO_3^{1-m}(aq) \rightarrow HSO_3 + CuX_n^{1-n}(aq),$$
$$CuX_m^{2-m}(aq) + HSO_3 + H_2O \rightarrow H_2SO_4 + CuX_n^{1-n}(aq) + H^+;$$

(b) second pathway [associated with the activation of HSO_3^- anions by copper(I)]:

$$Cu_2X_{(n+m)}HSO_3^{2-m-n}(aq) \rightarrow 2CuX_n^{1-n}(aq) + HSO_3.$$

In the reduction of copper(II) by sulphur dioxide in the presence of iodide ions, there is a possibility of electron transfer to the central atom and the formation in the inner sphere of the ligand I^0, which oxidises the HSO_3^- anion to HSO_3:

(a) first pathway:

$$CuX_mI(HSO_3)^{m-}(aq) \rightleftharpoons CuX_m(I^0)(HSO_3)^{m-}(aq),$$
$$CuX_m(I^0)(HSO_3)^{m-}(aq) \rightarrow HSO_3 + CuX_n^{1-n}(aq) + I^-;$$

(b) second pathway [associated with the activation of HSO_3^- anions by copper(I)]:

$$Cu_2X_{(m+n)}I(HSO_3)^{1-m-n}(aq) \rightleftharpoons Cu_2X_{(m+n)}(I^0)(HSO_3)^{1-m-n}(aq),$$
$$Cu_2X_{(m+n)}(I^0)(HSO_3)^{1-m-n}(aq) \rightarrow HSO_3 + 2CuX_n^{1-n}(aq) + I^-.$$

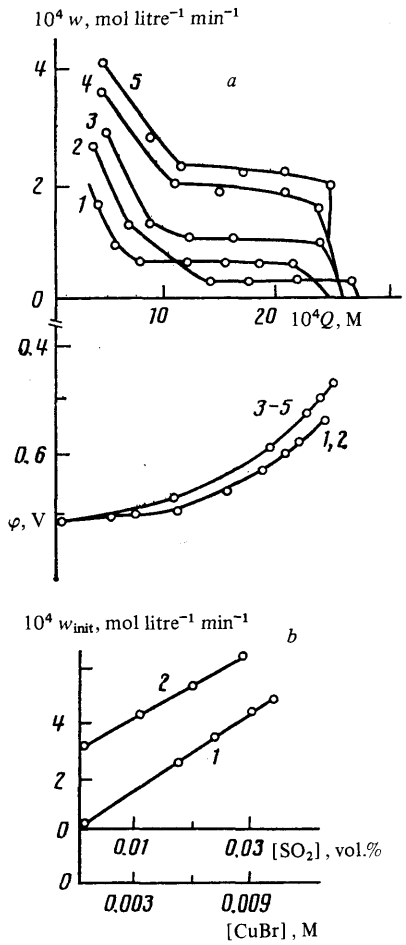


Figure 2. Oxidation of SO_2 by copper(II) bromide at 293 K, [HBr] = 6.0 M, and [KI] = 0.5 × 10^{-3} M: (a) dependence of the rate of oxidation w and of the potential of the system φ on the amount of SO_2 which has reacted for [$CuBr_2$] = 0.005 M and different initial SO_2 concentrations (vol.%) [(1) 0.017; (2) 0.023; (3) 0.028; (4) 0.032; (5) 0.035]; (b) dependence of the initial rate of oxidation on [SO_2] (line 1) for [$CuBr_2$] = 0.005 M and on [CuBr] (line 2) for [$CuBr_2$] = 0.003 M and [SO_2] = 0.028 vol.%.[18]

This scheme explains the catalytic action of the I^- ion (first order with respect to I^-), which served as a "mediator" in the electron transfer from SO_2 to Cu^{2+}. Bearing in mind that the reduction of copper(II) by sulphur dioxide in the $CuBr_2-LiBr-H_2O$ system in the presence of bromide ions alone, takes place at high concentrations of the latter, [Br^-] = 2–8 M and [Cu^{2+}] ≪ [Br^-], we suggest that homoligand copper(II) bromide complexes are the catalysts in this process. The activity of the chloride complexes in the SO_2 oxidation reactions has been observed only at a high sulphur dioxide concentration (100 vol.%).[32]

The rate of reduction of Cu^{2+} depends on the nature of the catalyst. The rate equation is[21]

$$w = (k_1 + k_2[Cu^+])[Cu^{2+}][SO_2],$$

where k_1 and k_2 are the rate constants for the first and second pathways respectively. Since the dependence of the rate of reduction of copper(II) by sulphur dioxide on the current copper(I) concentration is described by descending curves (Fig.1) of a non-autocatalytic character (the decrease in the rate of reaction as a result of the loss of Cu^{2+} is not compensated by its catalytic acceleration by the Cu^+ formed), one may conclude that the first pathway, unrelated to the activation of HSO_3^- anions by copper(I), makes the greatest contribution to the overall rate of the process. However, as a result of the existence of the second pathway, the kinetic curves do not obey a first-order equation with respect to CuX_2, while in the reduction of copper(II) bromide-iodide complexes, a "zero order" is observed over a large extent of the kinetic curves (Fig.2).[31]

Table 2. The activities of copper(II) halide complexes in the SO_2 oxidation reaction.[18,21,31]

Complex; system	k_1, litre mol^{-1} min^{-1}	k_2, litre^2 mol^{-2} min^{-1}	E_1, kJ mol^{-1}	E_2, kJ mol^{-1}	ΔS_1^*, J mol^{-1} K^{-1}	ΔS_2^*, J mol^{-1} K^{-1}
$CuBr_2I^-$ (aq); $CuBr_2$—HBr—KI—H_2O	$5.2\cdot10^2$	$7.7\cdot10^5$	28.8	46.0	—101	0.4
$CuCl_2I^-$ (aq); $CuCl_2$—HCl—KI—H_2O	$3.9\cdot10^2$	$1.7\cdot10^4$	32.6	24.7	—105	—90
$CuBr_3^-$ (aq)	$0.5\cdot10^{-2}$	4.5	44.0	40.0	—52	—5
$CuBr_2$ (aq); $CuBr_2$—LiBr—H_2O	$0.1\cdot10^{-2}$	0.5	—	—	—	—

Notation. k_1 and k_2 are the partial rate constants for the reaction, E_1 and E_2 are the apparent activation energies, and ΔS_1^* and ΔS_2^* are the activation entropies for the first and second pathways respectively.

Calculations and experimental results have shown that complexes with a definite composition of the inner sphere exhibit the highest activity in the reduction of copper(II) by sulphur dioxide. It follows from Table 2 that copper(II) halide complexes can be arranged in the following sequence in terms of their activities:

$$CuBr_2I^-(aq) > CuCl_2I^-(aq) > CuBr_3^-(aq) > CuBr_2(aq).$$

The activation energy for the first stage, which makes the greatest contribution to the overall rate of the process, increases on passing from the bromide-iodide complexes to the chloride complexes and further to the bromide complexes, which is consistent with the reaction rate constants.

The highest activation entropy ($\Delta S_2^* = 0.4$ J mol^{-1} K^{-1}) has been observed for the most active complex $CuBr_2I^-$(aq.) in the $CuBr_2-HBr-KI-H_2O$ system, indicating a high probability of the optimum orientation of the species at the instant of collision.

An appreciable catalytic acceleration of the oxidation of SO_2 by Cl^- and Br^- anions has been observed in a study[33] where the effect of certain anions and cations (Na^+, K^+, NH_4^+, Ca^{2+}, SO_4^{2-}, HCO_3^-, NO_3^-, F^-, Cl^-, Br^-) on the rate of oxidation of sodium sulphite was investigated. A significant cationic effect was not observed and Cl^- and Br^- ions showed an activity at concentrations above 1×10^{-3} M. The insignificant influence of the nature of the cation (Na^+, K^+, NH_4^+) on the oxidation of sulphite anions has also been noted in another study.[34]

It has been observed that the addition of iron chloride to the $CuCl_2-HCl-KI-H_2O$ system significantly increases the rate of oxidation of sulphur dioxide.[22,23] Kinetic and spectroscopic data have led to the conclusion that in the presence of chloride and iodide ions copper(II) and iron(III) form the heteronuclear complexes $CuFeCl_mI^{4-m}$(aq.), which are more active in the reaction with sulphur dioxide than the individual copper and iron complexes. The calculated stability constant of the heteronuclear complex is $\alpha = [Cu^{2+}-Fe^{3+}]/[Cu^{2+}][Fe^{3+}] = 10$.

The reduction of heteronuclear copper(II) and iron(III) complexes by sulphur dioxide also proceeds via two pathways. The reaction by the first pathway, which makes a greater contribution to the overall rate of the process, involves the inner-sphere oxidation-reduction decomposition of these complexes with the HSO_3^- anion in accordance with the equation[22,23]

$$CuFeCl_mIHSO_3^{3-m}(aq) + H_2O \rightarrow CuFeCl_n^{1-n}(aq) + H_2SO_4 + I^- + H^+. \quad (4)$$

The reaction via the second pathway is accelerated as a result of the activation of HSO_3^- anions by copper(I).

The kinetic equation describing the reduction of heteronuclear complexes is

$$w = [Cu^{2+}][Fe^{3+}]^{0.5}[SO_2](k_1 + k_2[Cu^+]),$$

where k_1 and k_2 are the rate constants for the first and second pathways respectively.

An attempt has been made to establish the composition of the heteronuclear complexes corresponding to the formula $CuFeCl_nI^{4-n}$ by the method of isomolar series [continuous variations (Editor of Translation)] (Fig.3).[22,23] The fact that the rate of reaction is a maximum for the ratio $[CuCl_2]:[FeCl_3] = 1:1$ suggested that one Cu^{2+} ion is bound to one Fe^{3+} ion in the active complex.

The existence of heteronuclear complexes in the $CuCl_2-FeCl_3-HCl-KI-H_2O$ system has been confirmed by calorimetric molar ratios and relative yield methods.[23] The formation of heteronuclear complexes is also indicated by the decrease in the intensity of the EPR signal of the $CuCl_2-HCl-KI-H_2O$ solution after the addition of $FeCl_3$ to the latter, demonstrating a decrease in the concentration of the $CuCl_2$ salt as a result of the formation of a heteronuclear complex which does not generate an EPR signal.[23]

In reaction (4), two individual complexes (copper and iron halides) exhibit a synergistic effect. A similar effect has also been observed in the oxidation of sulphur dioxide in aqueous solution by mixtures of manganese and iron salts. The most pronounced effect has been attained in a solution containing 1×10^{-4} M manganese acetate and 1×10^{-6} M iron chloride.[35]

The reason for the acceleration of the S(IV)–S(VI) oxidation is apparently the replacement of the two-stage electronic oxidation of SO_2 by the individual complexes under these conditions by a two-electron single-stage reaction, i.e. the redox process becomes synchronous.

Analysis of the experimental and literature data[18,21-25,31] leads to the conclusion that the reduction of metal complexes by sulphur dioxide proceeds via the formation of an intermediate–the metal complex with the hydrogen sulphite anion, in which the inner-sphere electron transfer from S^{4+} to M^{n+} takes place. It has been established that the components of systems incorporating metal complexes, sulphur dioxide, water, and ligands react in stoichiometric proportions, which rules out a chain mechanism of the reaction.[18,21-25,31]

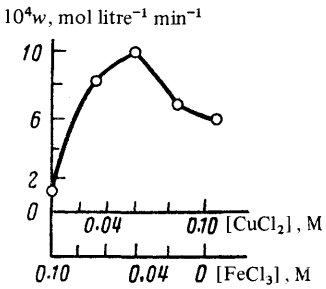


Figure 3. Dependence of the initial rate of reaction on the ratio $[CuCl_2]$: $[FeCl_3]$ at 293 K; [HCl] = 4.8 M; [KI] = 8×10^{-4} M; $[SO_2]$ = 0.58 vol.%.[23]

The electrochemical oxidation reactions of sulphites and SO_2, which readily occur on platinum and graphite anodes, are also of theoretical and practical importance. Thus the study of the anodic oxidation of H_2SO_3 on a platinum electrode showed that the overall rate of the process is determined by the oxidation of the reductant by oxygen from the water adsorbed electrochemically on platinum.[36] The process mechanism can be described by the following scheme:

$$Pt + H_2O - 2e \rightarrow PtO + 2H^+,$$
$$PtO + SO_3^{2-} \rightarrow Pt + SO_4^{2-},$$
$$PtO + SO_2 + H_2O \rightarrow Pt + H_2SO_4.$$

The rate of oxidation of sulphite anions falls appreciably as the bond between oxygen and the surface is strengthened.[37]

In order to increase the rate of reaction, the activation of the surface of the platinum is essential. It has been observed that the electrocatalytic activity of platinum in the presence of potassium iodide is several times higher than that of platinum merely coated by the SO_2H species.[38] It is assumed that the I_{ads} species on the surface participate in electron transfer across the interface. Apparently, both in the homogeneous systems described before and on the surface of electrode-catalysts, the mechanism of catalysis by the $I^0 + I^-$ pair is similar.

The adsorption of H_2SO_3 on electrodes used as electrocatalysts has also been studied in detail.[39-43] The electrochemical oxidation of sulphur dioxide on platinum–gold alloys and on organic metal complexes deposited on pyrographite or carbon black has been described.[44-46] One of the interesting applications of the electrochemical oxidation reaction involves its use in the thermoelectrochemical sulphuric acid method of preparation of hydrogen.

Studies in recent years have shown that not only platinum and platinum–carbon electrodes but also metalloporphyrin electrodes can be used as electrode-catalysts.[47–49]

The electrochemical oxidation of sulphur dioxide, which does not require oxidants, is apparently of interest for the elimination of SO_2 from gases.[50]

III. CATALYTIC REACTIONS INVOLVING THE OXIDATION OF SO_2 BY MOLECULAR OXYGEN

Studies on processes involving the oxidation of sulphur dioxide by molecular oxygen in the presence of homogeneous catalysts and water are of practical interest.

$$SO_2 + {}^1/_2O_2 + H_2O \xrightarrow{\text{catalyst}} H_2SO_4.$$

This reaction has been used since the past century for the preparation of H_2SO_4 by the familiar chamber method which has been described in many publications (see, for example, Amelin and Yashke[51]). However, a mechanism fundamentally different from the classical mechanism has been proposed comparatively recently.[52] All the versions of the traditional mechanism of the chamber process postulate the involvement of sulphuric acid in the form of nitrosylsulphuric acid in the sulphur dioxide oxidation step,[51] although under the experimental conditions the maximum rate of reaction in acid solutions is observed in the absence of H_2SO_4, an increase in the H_2SO_4 concentration inhibiting the reaction.[52]

The $SO_2-H_2O-HNO_3-O_2$ system has been investigated at 363–448 K and SO_2 pressures from 2×10^5 to 8×10^4 Pa.[52] The authors believe that the active oxidising species (oxygen transferring agent) is the nitronium ion NO^+ and it is postulated that the oxygen transfer to sulphurous acid molecules is effected not by the free nitronium ions but by their complexes with sulphite ions. The sulphur dioxide oxidation mechanism is described by the scheme:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^-,$$
$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O,$$
$$HSO_3^- + NO_2^+ \rightleftharpoons HSNO_5,$$
$$HSNO_5 + H^+ \rightarrow H_2SN^{\text{V}}O_5 \rightarrow (H_2SO_4)N^{\text{V}}O,$$
$$(H_2SO_4)N^{\text{V}}O \xrightarrow{HSO_3^-;\ O_2} H_2SO_4 + (HSO_3^-)N^{\text{V}}O \rightarrow HSNO_5.$$

Sulphur dioxide is oxidised by molecular oxygen under similar conditions in an aqueous medium using particles of activated charcoal as the catalyst, although it is assumed that in this case the process proceeds via a mechanism different from that of the oxidation of SO_2 in the presence of metal complexes.[53] The reaction is of first order with respect to the catalyst suspended in solution and with respect to molecular oxygen. The order with respect to SO_2 varies from 0 to 2 and the rate of the process is independent of the pH of the solution.[54]

In a study of the kinetics of the oxidation of sulphur dioxide by molecular oxygen in aqueous solutions containing vanadium salts, it has been established that in this case V^{5+} ions initiate the chain reaction:[55]

$$VO_2^+ + SO_3^{2-} + 2H^+ \rightleftharpoons VO^{2+} + \dot{S}O_3^- + H_2O.$$

The process then develops in accordance with the scheme

$$\dot{S}O_3^- + O_2 \rightarrow \dot{S}O_5^-,$$
$$\dot{S}O_5^- + SO_3^{2-} \rightarrow SO_5^{2-} + \dot{S}O_3^-,$$
$$SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-}.$$

Chain termination takes place as a result of radical recombination. The equation describing the rate of formation of sulphuric acid is

$$w = k([O_2][SO_2][V]^{1/4})/[H_2SO_4]^2.$$

The oxidation of sulphur dioxide by molecular oxygen in aqueous solutions containing $Fe_2(SO_4)_3$ has been investigated in the absence and presence of V^{4+}.[56] In the former case, a chain reaction mechanism is also postulated:

$$Fe^{3+} + SO_3^{2-} \rightarrow Fe^{2+} + \dot{S}O_3^-,$$
$$\dot{S}O_3^- + O_2 \rightarrow \dot{S}O_5^-,$$
$$Fe^{2+} + \dot{S}O_5^- \rightarrow Fe^{3+} + SO_5^{2-},$$
$$SO_3^{2-} + SO_5^{2-} \rightarrow 2SO_4^{2-}.$$

The rate of reaction is expressed by the equation

$$w = 4.32 \times 10^7 \exp(9625/RT)[SO_2].$$

V^{4+} ions lower the rate of reaction because they interact with the $\dot{S}O_5^-$ radical-ions, diminishing their concentration.

The oxidation of sulphur dioxide by molecular oxygen in the presence of iron salts has also been studied by Freiberg,[57] who established that the reaction order with respect to Fe^{3+} increases from 0 to 1 with decrease in $[Fe^{3+}]$. The oxidation of sulphur dioxide by Fe^{3+} ions competes with its catalytic oxidation by molecular oxygen at $[Fe^{3+}] > 2 \times 10^{-3}$ M. The author quotes two equations describing the variation of the overall rate of reaction with increase in pH and in the sulphur dioxide concentration.

In contrast to Bronikowski,[56] Freiberg[57] postulates a non-radical mechanism of the oxidation of sulphur dioxide:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-},$$
$$Fe(OH)^{2+} + H^+ \rightleftharpoons Fe^{3+} + H_2O,$$
$$Fe^{3+} + HSO_3^- \rightleftharpoons Fe(HSO_3)^{2+},$$
$$Fe(HSO_3)^{2+} + SO_3^{2-} \rightleftharpoons Fe(HSO_3)(SO_3),$$
$$Fe(HSO_3)(SO_3) + O_2 + H_2O \rightarrow Fe(OH)^{2+} + 2HSO_4^-,$$
$$Fe(HSO_3)(SO_3) + Fe^{3+} + H_2O \rightarrow 2Fe^{2+} + HSO_4^- + HSO_3^- + H^+.$$

Lunak et al.[58] likewise adhere to the view that the oxidation of sulphur dioxide by molecular oxygen in the presence of copper(II), iron(III), cobalt(III), nickel(II), and manganese(II), salts cannot be described by a radical-chain mechanism and propose an associative mechanism, according to which relatively stable complexes are formed between sulphite anions and the catalyst. The possibility of the formation of complexes between S(IV) and M^{x+} in the oxidation of SO_2 by molecular oxygen has also been indicated by Beilke and Gravenhorst.[59]

It has been established[58] that the oxidation of sulphur dioxide by molecular oxygen is of first order with respect to SO_2 over a wide range of concentrations of the latter. The catalytic action of transition metal ions on the reaction decreases in the sequence

$$Fe^{2+} \simeq Co^{2+} > Mn^{2+} \simeq Cu^+,\ Cu^{2+} \gg Fe^{3+} \simeq Co^{3+} \gg Ni^{2+}.$$

In the oxidation of SO_2 by molecular oxygen in the presence of Fe^{2+} in the pH range 0.8–5.0 in solutions, the reaction has an induction period whose duration increases with increase in the acidity of the medium.[60] It has been observed that, in the oxidation of sulphur dioxide by molecular oxygen, the addition of Mn^{2+} and Fe^{3+} has a comparatively small influence on the rate of the process.[61] On the other hand, other investigators regard manganese(II), iron(III), and also cobalt(II) compounds as promising catalysts of this reaction.[62–66] It has been established that iron and

manganese salts are active in a comparatively acid medium, while cobalt salts are active only in an alkaline medium. The maximum activity is observed at pH ~3.4 (Fe), 4.1 (Mn), and 9.0 (Co).[62,63] A radical-chain mechanism of the catalytic oxidation of SO_2 has been proposed in the above studies. In the oxidation of sulphur dioxide in acid solutions, the chains are short (n = 1, 2) and the reaction order with respect to SO_2 is close to or greater than unity and that with respect to the catalyst is less than unity. In alkaline solutions, the chains are lengthened and the reaction order is 1.5 with respect to SO_2 and 0.5 with respect to the catalyst.

It has been suggested[64] that the oxidation of SO_2 by molecular oxygen in the presence of $MnSO_4$ proceeds in accordance with the scheme

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-},$$

$$\left.\begin{aligned} Mn^{3+} + HSO_3^- &\rightarrow Mn^{2+} + \dot{H}SO_3 \\ Mn^{3+} + HSO_3^- &\rightarrow Mn^{2+} + \dot{H}SO_3 \end{aligned}\right\} \text{initiation},$$

$$\left.\begin{aligned} \dot{H}SO_3 + O_2 &\rightarrow \dot{H}SO_5 \\ \dot{H}SO_5 + HSO_3^- &\rightarrow HSO_5^- + \dot{H}SO_3 \end{aligned}\right\} \text{chain propagation},$$

$$\left.\begin{aligned} \dot{H}SO_5 + \dot{H}SO_3 &\rightarrow; \quad 2\dot{H}SO_5 \rightarrow; \quad 2\dot{H}SO_3 \rightarrow \\ \dot{H}SO_3 + Mn^{3+} &\xrightarrow{H_2O} H_2SO_4 + Mn^{2+} + H^+ \end{aligned}\right\} \text{chain termination},$$

$$\left.\begin{aligned} \dot{H}SO_5 + Mn^{2+} &\rightarrow HSO_5^- + Mn^{3+} \\ 2Mn^{2+} + HSO_5^- &\xrightarrow{2H^+} 2Mn^{3+} + HSO_4^- + H_2O \end{aligned}\right\} \text{regeneration of } Mn^{3+} \text{ ions},$$

$$Mn^{2+} \rightarrow Mn^{3+} \quad \text{autoxidation}.$$

The scheme also includes other reactions, for example:

$$HSO_5^- + HSO_3^- \rightarrow 2HSO_4^-.$$

A radical-chain mechanism of the oxidation of SO_2 by molecular oxygen has been likewise proposed for catalysis by Co^{2+} [67] and Fe^{2+} [68] ions. The reaction catalysed by Fe^{2+} has an induction period whose duration increases with increasing acidity of the medium.[69] In aqueous solutions at pH 8.5, the catalytic action of Co^{2+} ions is 12 times stronger than that of Cu^{2+} ions.[67] The reaction orders with respect to O_2, Co^{2+}, and SO_2 are respectively 0, 0.5, and 1.5, while in another study[70] a reaction order with respect to O_2 equal to unity has been quoted for analogous conditions.

The oxidation of sulphur dioxide by molecular oxygen in the presence of copper(I, II) halides has been studied in the $CuCl_2-HCl-KI-H_2O$ and $CuBr_2-KI-H_2O$ systems.[71,72] It was found that the process consists of two stages: the reaction involving the reduction of copper(II) by sulphur dioxide in accordance with Eqn.(3) and the reaction in which copper(I) is oxidised by molecular oxygen:

$$4CuX + O_2 + 4HX \rightarrow 4CuX_2 + 2H_2O. \qquad (5)$$

The rate of oxidation of sulphur dioxide by molecular oxygen can in general depend on the ratio of the rate constants for reaction (3) and (5), while under the conditions of the experiments of Golodov et al.[72] it is described by reaction (5).

Fig.4[71,72] presents typical kinetic and potentiometric curves for the oxidation of SO_2 by molecular oxygen. There are two sections on these curves: non-stationary and stationary. Along the non-stationary section, Cu^{2+} is reduced via reaction (3). Under stationary conditions, equilibrium is established between the reactions involving the reduction of Cu^{2+} by sulphur dioxide [reaction (3)] and the oxidation of Cu^+ by molecular oxygen [reaction (5)]. In order to increase the overall rate of oxidation of sulphur dioxide by molecular oxygen, it is necessary to use factors accelerating the oxidation of Cu^+ to Cu^{2+}, which is then rapidly reduced to Cu^+. Calculations have shown[71,72] that the $CuCl_3^{2-}$(aq.) complex in the $CuCl_2-HCl-KI-H_2O$ system and the $CuBr_3^{2-}$(aq.) complex in the $CuBr_2-HBr-KI-H_2O$ system have the highest activity in the reactions where Cu^+ is oxidised by molecular oxygen.

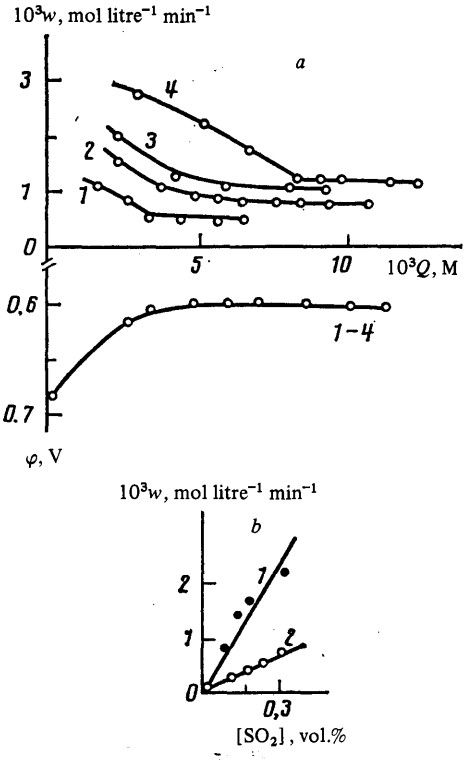


Figure 4. Oxidation of SO_2 by molecular oxygen at 293 K, $[CuCl_2]$ = 0.02 M, [HCl] = 4.8 M, [KI] = 8×10^{-4} M, and $[O_2]$ = 20 vol.%: (a) dependence of the rate of reaction and of the oxidation-reduction potential of the system on the amount of SO_2 which has reacted at different SO_2 concentrations (vol.%) [(1) 0.06; (2) 0.14; (3) 0.17; (4) 0.26]; (b) dependence of the initial (line 1) and stationary (line 2) rates of reaction on $[SO_2]$.[71]

The rate of oxidation of Cu^+ by molecular oxygen is described by the equation

$$w = k_{st}[Cu^+]_{st}[SO_2][O_2],$$

where k_{st} and $[Cu^+]_{st}$ are respectively the rate constant and the concentration of Cu^+ in the stationary region.

Iodide ions do not influence the oxidation of Cu^+. Thus the highest activity in the oxidation of sulphur dioxide by molecular oxygen is shown by copper chloride-iodide complexes. Along the non-stationary section, the reaction is of first order with respect to Cu^{2+}, SO_2, and I^-, while along the stationary section it is of first order with respect to Cu^+, SO_2, and O_2.[71,72] The addition of iron chloride to the $CuCl_2-HCl-KI-H_2O$ system greatly increases the rate of reaction along the non-stationary and stationary sections.[23]

The results of the study by Hegg and Hobbs[73] also show that catalysis by mixtures of iron, copper, and manganese salts leads to a tenfold increase in the rate of oxidation of sulphur dioxide by molecular oxygen compared with the rate of oxidation in the presence of a one-component catalyst alone. The oxidation of SO_2 by molecular oxygen in the presence of copper(I, II) halides and variable-valence metal salts (Mn, Fe) is inhibited by phenolic antioxidants and chelating additives[74] and also by surfactants.[75]

Studies on sulphur dioxide oxidation processes in air are of great theoretical and practical interest.[61,76,77] It has been observed that SO_2 is oxidised in air via several pathways:[61] (a) non-catalytic oxidation by molecular oxygen; (b) oxidation by molecular oxygen in the presence of metallic catalyst particles; (c) oxidation by O_3, H_2O_2, and SO_2; (d) oxidation in the presence of NH_3 acting as a neutralising agent.

The contributions of the principal mechanisms of the oxidation of SO_2 in air to the overall conversion of sulphur dioxide have been examined.[77] The overall contribution of the photochemical formation of excited sulphur dioxide molecules and of their interaction with O_2, O_3, and H_2O_2 as well as the reaction of SO_2 with the $\dot{O}H$, $\dot{R}O_2$, and $\dot{H}O_2$ radicals reaches 9%. The liquid-phase oxidation in the water droplets in clouds reaches 35%. The rate of this process is influenced by the pH of the drops, by the presence of metal ions (Fe and Mn), and by the presence of oxidants other than O_2 (O_3, H_2O_2). The contribution by the gas-phase oxidation of SO_2 with subsequent removal of sulphates from the atmosphere in the form of aqueous solutions is 50% of the overall balance. The remaining SO_2 is removed in the form of solid deposits.

The mechanism of the oxidation of sulphur dioxide in the atmosphere in the presence of metal ions includes the following stages:[78]

$$SO_3^{2-} + M^{+} \rightleftharpoons \dot{S}O_3^{-} + M \quad \text{initiation},$$

$$\left.\begin{aligned} &\dot{S}O_3^{-} + O_2 \rightleftharpoons \dot{S}O_5^{-},\\ &\dot{S}O_5^{-} + HSO_3^{-} \rightleftharpoons HSO_5^{-} + \dot{S}O_3^{-} \quad (pH \lesssim 7)\\ &\dot{S}O_5^{-} + SO_3^{2-} \rightleftharpoons SO_5^{2-} + \dot{S}O_3^{-} \quad (pH \gtrsim 7) \end{aligned}\right\} \text{chain propagation},$$

$$\left.\begin{aligned} SO_3^{2-} + HSO_5^{-} &\rightleftharpoons HSO_4^{-} + SO_4^{2-} \quad (pH \lesssim 7)\\ SO_3^{2-} + SO_5^{2-} &\rightleftharpoons 2SO_4^{2-} \quad (pH \gtrsim 7) \end{aligned}\right\} \text{oxidation},$$

$$\left.\begin{aligned} &\dot{S}O_3^{-} + \dot{S}O_5^{-} \rightleftharpoons S_2O_8^{2-} + O_2\\ &\dot{S}O_5^{-} + \text{inhibitor} \rightleftharpoons \text{inactive product} \end{aligned}\right\} \text{destruction of radicals}.$$

In conclusion, we shall consider the photochemical oxidation of sulphite anions. This reaction in the absence and presence of molecular oxygen has been described in detail.[79] Sulphates are formed in the absence of O_2 as a result of the oxidation of monothionic acid HSO_3, which is the primary product in the irradiation of the sulphite products by visible light,

$$SO_3^{2-} + H_2O \xrightarrow{h\nu} SO_3^{-} + H + OH^{-},$$
$$SO_3^{-} + H^{+} \rightarrow HSO_3 \ (H^{+}\text{—from water}),$$
$$HSO_3 + H + H_2O \rightarrow H_2 + H_2SO_4.$$

In the presence of molecular oxygen, sulphates are formed in accordance with the equation

$$HSO_3 + O_2 + SO_3^{2-} \rightarrow 2SO_4^{2-} + H.$$

Thus the photochemical activation of SO_2 leads to the formation of sulphuric acid vapour in the atmosphere.[80] The acid is then removed from air with rain drops—this is the main pathway leading to the natural elimination of SO_2 from the atmosphere.[81]

It follows from the present review that at the present time there is no unanimous view concerning the mechanism of the oxidation of SO_2 in aqueous solutions; radical-chain and associative mechanisms have been proposed. The adherents of the radical-chain mechanism believe that radicals may be formed in the interaction of sulphite anions with metal ions in accordance with the equation

$$SO_3^{2-} + M^{n+} \rightleftharpoons \dot{S}O_3^{-} + M^{n-1}$$

or as a result of the reactions[55,56,83]

$$2HSO_3^{-} \rightleftharpoons S_2O_5^{2-} + H_2O,$$
$$S_2O_5^{2-} \rightleftharpoons \dot{S}O_3^{-} + \dot{S}O_2^{-}.$$

The associative mechanism includes the formation of relatively stable complexes between sulphite anions and the catalyst.[58,84]

Analysis of the literature data shows that the stoichiometry of the oxidation of sulphur dioxide by metal complexes, i.e.

$$SO_2 + 2M^{n+} + 2H_2O \rightarrow H_2SO_4 + 2M^{n-1} + 2H^{+}$$

is satisfied, which rules out the chain reaction pathway.

It is most likely that the oxidation of sulphur dioxide by metal complexes proceeds via the formation of an intermediate compound of M^{n+} with the hydrogen sulphite anion formed via reaction (6), because the HSO_3^{-} anion is a more active electron donor than SO_2:[82,85]

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons HSO_3^{-} + H^{+}. \qquad (6)$$

The subsequent reactions in the system can be represented by the following scheme:

$$HSO_3^{-} + M^{n+}(aq) \rightleftharpoons MHSO_3^{n-1}(aq) + H_2O, \qquad (7)$$

$$MHSO_3^{n-1}(aq) \rightleftharpoons M^{n-1}(aq) + HSO_3, \qquad (8)$$

$$M^{n+}(aq) + HSO_3 + H_2O \rightarrow H_2SO_4 + M^{n-1}(aq) + H^{+}. \qquad (9)$$

The HSO_3^{-} anion interacts via reaction (7) with the metal complex, whereupon the intermediate $MHSO_3^{n-1}$(aq.) appears and then undergoes the inner-sphere redox reaction (8) with the formation of monothionic acid HSO_3. The possibility of the formation of HSO_3 during the reaction has also been pointed out in other studies.[86,87] In the next stage [reaction (9)], monothionic acid is oxidised rapidly to H_2SO_4.

The oxidation of SO_2 via a chain mechanism is also possible in processes with photochemical and radiochemical activation of the molecules of sulphur dioxide and molecular oxygen.[88-90]

IV. CONCLUSION

The problem of the search for and study of effective catalysts of the oxidation of sulphur dioxide to sulphuric acid, including liquid-phase oxidation, continues to be of interest. Special interest attaches to the elucidation of the process mechanism and of the influence of a number of factors on the kinetics of individual stages of the complex reaction, which promotes the development of promising and economical catalysts.

According to Dorfman,[82] the optimum system for the liquid-phase oxidation of sulphur dioxide by molecular oxygen should contain

the following components: (1) electron donors capable of intensifying the electron-donating function of the sulphur dioxide molecule; (2) halogens which interact with the donor orbital of the SO_2 molecule; (3) a polar solvent and a metal ion which give rise to stable compounds together with a halogen cation or halide anion and increase thereby the dipole moment of the halogen molecule; (4) a variable-valence metal ion, which reacts rapidly with molecular oxygen. The $CuCl_2-HCl-KI-H_2O$ and $CuCl_2-FeCl_3-HCl-KI-H_2O$ systems satisfy these features.[21,23]

The liquid-phase oxidation of SO_2 to H_2SO_4 has already found a practical application: the use of homogeneous catalysts for the elimination of the sulphur dioxide impurity from waste gases in various industries has been described.[91,92] Tests on catalysts based on copper and iron halide salts have shown that, for a high space velocity of the effluent gas (12 000 h^{-1}), the degree of conversion reaches 98% and the residual content of sulphur dioxide is 0.003 to 0.01 vol.%.[92] The 50% acid obtained, containing copper and iron complexes, can be used for the treatment of oxidised copper ores, which makes it possible to reduce the consumption of commercial sulphuric acid. Furthermore, the elimination of toxic sulphur dioxide from the effluent gas greatly improves the ecological position.

The choice of the method for the extraction and processing of sulphur dioxide is determined mainly by its concentration in the gas. Comparatively concentrated, with $[SO_2] > 4\%$, effluent gases in the non-ferrous metallurgy—roasting, converter and water jacket gases—can be used to manufacture sulphuric acid by the chamber or contact (in the presence of vanadium catalysts) method. Data have been published recently concerning the possibility of using heterogeneous catalysts also for gases at low concentrations.[2,93]

The temperature range of the operation of vanadium catalysts is in the region of high temperatures (400–600 °C). Practice has shown that their activity falls during use as a function of the nature of the sulphur-containing raw material, the degree of purification and variations in the concentration of sulphur dioxide, and the temperature range and the presence of catalyst poisons—arsenic and fluorine.[94,95] Gases with a low sulphur content (from 1 vol.% SO_2 upwards) have been utilised in recent years by employing non-stationary conditions.[96]

As shown above, the catalytic oxidation of SO_2 to H_2SO_4 in aqueous solutions takes place successfully also at a much lower SO_2 concentration in the effluent gases and under these conditions the method becomes economically viable. On comparing the liquid-phase homogeneous and heterogeneous catalytic methods for the oxidation of SO_2, it is possible to note the following advantages of the former: (1) homogeneous oxidation of SO_2 proceeds under mild conditions and does not require additional energy expenditures; (2) certain catalysts, for example, solutions of copper(II) halide salts, do not require additional elimination of arsenic and fluorine from the gas: F^- ions increase the rate of oxidation of SO_2 and As^{3+} is readily oxidised by copper(II); (3) waste water, containing active metal ions (Cu^{2+}, Fe^{3+}, Mn^{4+}, Mn^{7+}), can be used for the sanitary purification of gases.

Among the disadvantages of the method, one should include the corrosion activity of the catalytic solutions, the high concentration of halides in certain systems, the need to eliminate metal ions from the H_2SO_4 obtained, and the low final concentration of this acid (50 wt.%).

Thus the study of the processes leading to the oxidation of SO_2 to sulphuric acid in aqueous solutions is not only of theoretical interest but also helps to solve the problem of the purification of effluent gases.

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The Synthesis and Properties of Covalent Organic Perchlorates

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The review is devoted to the chemistry of perchloric acid esters—a relatively little investigated class of compounds with exceptionally interesting properties. Data on the methods of synthesis and reactivities of covalent organic perchlorates are described systematically and surveyed.
The bibliography includes 141 references.

CONTENTS

I. Introduction 1041
II. Methods of synthesis 1041
III. Properties 1048

I. INTRODUCTION

During the last 30 years, there has been a sharp increase of interest in perchloric acid and its derivatives. Inorganic and organic compositions based on perchlorates have found extensive applications as rocket fuel and explosives, industrial catalysts, drying agents, accumulator electrolytes, etc.[1] Perchloric acid and perchlorates have come to be widely used in scientific research in analytical, physical, and organic chemistry. The growing interest in perchlorates has been expressed in a fairly large number of publications appearing annually in the periodical literature. However, the vast majority of these studies are concerned with perchlorates having ionic structures—inorganic and organic salts of perchloric acid. Although the first covalent perchorate, ethyl perchlorate, was obtained as early as 1841,[2] the chemistry of compounds of this class has developed very slowly until recently; thus at best 1–2 pages have been devoted to them in the two existing reviews[3,4] and monographs.[1,5]

The reason for this is evident—perchloric acid esters are mostly relatively unstable and extremely explosive substances, which makes working with them very difficult. However, spectroscopic identification methods which have been developed during the last 20 years as well as the technique involving experiments at low temperatures with microamounts of substances have made it possible to reduce the risk in studies in this field to a minimum. Furthermore, there has been a growth of interest in the possible practical applications of covalent organic perchlorates as alkylating agents[6] and polymerisation catalysts.[7-10] These factors as well as the evident theoretical interest which the highly reactive covalent perchlorates represent has led many investigators in recent years to search for new ways of synthesising perchloric acid esters. Among the advances in this field, we may mention the discovery of the phenomenon of the competitive binding of nucleofugitive anions, including ClO_4^-, in carbonium ion processes which have made it possible to extend sharply the range of perchlorates synthesised.

The synthesis of a large set of relatively stable covalent perchlorates, namely arenesulphonylmethyl perchlorates,[11] perfluoroalkyl perchlorates,[12,13] certain skeletal perchlorates,[14-17] as well as silyl perchlorates,[18] may be mentioned as a considerable advance in the chemistry of perchlorates during the last 10–15 years, which has allowed a more thorough investigation of the reactivity of compounds of this interesting class. Furthermore, the development of kinetic measurement techniques made it possible to investigate the detailed mechanisms of the reactions of a series of highly reactive unstable perchlorates.[19-22] All these factors have made it urgently necessary to carry out an exhaustive survey of the literature data on covalent perchlorates and to analyse in detail both the results obtained and the prospects for the development of this branch of organic chemistry. The present review is devoted to this problem; it covers the entire available literature on the synthesis and properties of covalent perchlorates up to 1986 and is the first exhaustive survey of this field.

II. METHODS OF SYNTHESIS

1. General Principles of the Synthesis of Perchloric Acid Esters

One of the simplest covalent perchlorates—ethyl perchlorate—has been obtained by distillation from a concentrated solution of the barium salts of ethylsulphuric and perchloric acid:

$$Ba(RSO_4)_2 + Ba(ClO_4)_2 \rightarrow 2ROClO_3 + 2BaSO_4,$$
$$R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7.$$

The possibilities of this method for the synthesis of methyl, ethyl, and propyl perchlorates were later investigated;[23] in particular, the optimum temperature range for these reactions was discovered (170–200 °C). Despite the appreciable danger involved,[3,23] this method was until 1936 virtually the only procedure for the preparation of lower alkyl perchlorates.[23,24]

Progress in the synthesis of perchloric acid esters has been associated both with the introduction into practical organic synthesis of new inorganic reagents such as perchloric acid, chlorine pentoxide, silver perchlorate, and halogen perchlorates, and with a deeper understanding of the problem of nucleophilic reactivity as a whole.

Any ester of an inorganic acid ROX can be obtained, in principle, in two general ways. The first is based on the reaction of alcohols or their derivatives with the anhydride or halide of the given inorganic acid. In this method of synthesis of the inorganic acid ester, an oxygen–element bond is formed. When applied to covalent perchlorates, the method reduces to the reaction of alcohols and their derivatives with chlorine pentoxide or perchloryl fluoride:

$$ROH + Cl_2O_7 \rightarrow ROClO_3 + HClO_4,$$
$$ROH + FClO_3 \rightarrow ROClO_3 + HF.$$

At the present time, these reactions have been investigated in fair detail and will be examined below. On the whole, this is a fairly acceptable synthetic method, limited solely by the explosive properties of the reagents used, in particular, chlorine pentoxide.

The second general method of synthesis of esters of the type ROX is based on reactions in which the OX^- anion plays the role of the nucleophile attacking the electrophilic carbon atom; an oxygen–carbon bond is formed in this method of synthesis. When applied to the synthesis of covalent perchlorates, this means the use of the perchlorate anion ClO_4^- as the nucleophile:

$$\rangle C^+ + ClO_4^- \rightarrow \rangle C-OClO_3,$$

$$\rangle C-Y + ClO_4^- \rightarrow O_3ClO-C\langle .$$

The development of this approach was significantly restricted by the idea which arose at the beginning of the 1970s that the perchlorate anion has no nucleophilic properties. Indeed, attempts to measure the parameters of the nucleophilicity of ClO_4^- within the framework of the generally employed Swain–Scott[25] and Ritchie[26,27] scales were unsuccessful and estimates in terms of the two-parameter Edwards scale[28] provided grounds for the assumption that this anion is an ultra-weak nucleophile. This view is well reflected in the familiar textbook of Roberts and Caserio,[29] in which lithium perchlorate, a source of the perchlorate anion, is defined as a "non-nucleophilic substance". It is not fortuitous that perchloric acid salts, such as lithium perchlorate, are usually employed in connection with the study of salt effects, because these salts do not affect the course of the reaction by binding to the intermediate carbonium ion.[30–33]

It was believed previously that the covalent binding of the perchlorate anion, leading to covalent perchlorates, is possible only under specially created conditions: in the complete absence of other nucleophilic species and in media with a low polarity. On this basis, a number of methods were developed for the synthesis of covalent perchlorates, for example, by the reaction of alkyl halides with silver perchlorate or by the addition of halogen perchlorate to perfluoro-olefins (see below). A limitation of all these methods was the necessity to use exceptionally explosive or expensive reagents such as halogen perchlorates and silver perchlorate.

However, in recent years the authors of the present review found unexpectedly that the perchlorate ion can manifest nucleophilic properties also in the presence of extraneous nucleophiles (halide ions, AcO^-, AcOH, etc.).[14,15,34–36] This discovery (which applies also to other nucleofugitive anions as well as ClO_4^-—triflate, fluorosulphate, toluene-*p*-sulphonate, methanesulphonate, etc.[36]) made it possible to devise a series of new convenient methods of synthesis of covalent perchlorates having different structures. The methods developed are based on a wide range of carbonium ion processes such as electrophilic addition to olefins,[14,15,34–36] opening of epoxide rings,[36–40] deamination of amines,[34,41] chlorination of sulphides,[42] deoxygenation of alcohols by treatment with sulphur and chlorine,[43] oxidative substitution of iodine in alkyl iodides,[44,45] and the interaction of aryliodoso-derivatives with olefins.[46–48] Alkali metal perchlorates, which are safe to handle and are readily available, are used as the reagents in all these cases.

In conclusion of this Section, we may note that in the description below the data will be grouped in terms of the types of initial compounds rather than the reaction mechanisms; this arrangement of the material is dictated both by the synthetic bias of the present review and by the extremely scanty experimental data on the kinetics and mechanisms of the synthesis of covalent perchlorates.

2. Synthesis From Alcohols and Ethers

The synthetic possibilities of the reactions of alcohols with perchloric acid have been investigated in fair detail. The explosive character of the interaction of anhydrous perchloric acid with absolute ethanol was reported as early as 1936.[23] However, the reactions of polyhydric alcohols with perchloric acid take place more quietly and can be used for the preparative synthesis of perchloric acid mono- and poly-esters. Thus the esters of perchloric acid with ethylene glycol, glycerol, and pentaerythritol have been obtained by the direct interaction of the hydroxy-compounds with anhydrous perchloric acid, which plays the role of a powerful dehydrating agent in this reaction, forming a monohydrate.[49] The esterification was carried out by the cautious addition of the alcohol to an excess of perchloric acid at −78 °C, the mixture being subsequently maintained at 60–80 °C for 20–40 min. The isolation of the esterification products presented a special problem. It has been reported[49] that, when the reaction mixture is diluted directly with water, "enormously powerful explosions" take place, which are apparently a consequence of the very rapid heating on hydration of perchloric acid. This risk was avoided by diluting the reaction mixture initially with 70% perchloric acid. The subsequent addition of a large amount of water causes the precipitation of a deposit of the organic perchlorate in the form of a heavy oil (density in excess of 1.7) or flakes (in the case of pentaerythritol). The authors[49] had to design a special apparatus for the extraction of the perchlorates with ether because powerful explosions occurred in the usual separating funnel when the ethereal solution entered the ground joints.

A modification of the esterification of alcohols with perchloric acid was subsequently developed.[50] Here the reagent employed was a mixture comprising 70% of perchloric acid, concentrated sulphuric acid, and oleum or a solution of an alkali metal perchlorate in 96% sulphuric acid. The alcohol is added slowly to a vigorously stirred emulsion of the acid reagents with an inert organic solvent at a temperature between −10° and 25 °C. The rapidly formed covalent perchlorate is concentrated in the organic phase. The method[50] is suitable only for the synthesis of secondary perchlorates from the corresponding alcohols (yield 70–90%), whilst primary alcohols react very slowly with formation of isomeric secondary perchlorates. The reaction mechanism apparently involves the preliminary formation of alkyl sulphates, the generation of a carbonium ion, possible isomersiation, and binding to the perchlorate anion. The carbonium ion character of the process has been confirmed, in particular, by the formation of an identical 1:1 mixture of 2- and 3-hexyl perchlorates when the reaction was carried out with both 2-hexanol and 3-hexanol.

A convenient method of synthesis of covalent perchlorates by the interaction of alcohols with chlorine heptoxide has been proposed:[51]

$$ROH + O_3ClOClO_3 \rightarrow ROClO_3 + HClO_4.$$

Chlorine heptoxide was used in the form of a relatively safe solution in carbon tetrachloride[52] and the perchloric acid produced in the reaction was bound with sodium sulphate.

One of the attractive features of this reaction is the formation of perchlorates exclusively with a non-rearranged structure, on the basis of which it has been concluded[51] that the C–O bond is really not involved in this reaction. The method yields best results for primary alcohols and diols, while in the reactions with secondary alcohols the corresponding ketones are formed as side products (8–9%) together with the perchlorates. The wide variety of structures and

the yields of the covalent perchlorates in the reactions investigated are demonstrated by the data in Table 1. Baum and Beard[51] noted that they were unable to obtain t-butyl perchlorate, apparently because of the instability of this product. On the other hand, perfluoro-t-butyl perchlorate proved to be entirely stable and was obtained in 33% yield by the reaction of sodium alkoxide with chlorine pentoxide:[51]

$$(CF_3)_3CONa + Cl_2O_7 \rightarrow (CF_3)_3COClO_3 + NaClO_4.$$

Apart from the alcohols themselves, their alkoxides can also be used as starting materials, the role of the reagent being usually assumed in this instance by perchloryl fluoride:[53]

$$RO^-M^+ + FClO_3 \rightarrow ROClO_3 + MF,$$
$$M = Na,\ (NH_2)_3C.$$

Table 1. The yields of covalent perchlorates in the reactions of alcohols with chlorine heptoxide in carbon tetrachloride (according to Baum and Beard's data[51]).

Initial alcohol	Perchlorate obtained	Yield, %
CH_3OH	CH_3OClO_3	42
C_2H_5OH	$C_2H_5OClO_3$	56
$n\text{-}C_3H_7OH$	$n\text{-}C_3H_7OClO_3$	73
$n\text{-}C_4H_9OH$	$n\text{-}C_4H_9OClO_3$	71
$n\text{-}C_5H_{11}OH$	$n\text{-}C_5H_{11}OClO_3$	63
$n\text{-}C_6H_{13}OH$	$n\text{-}C_6H_{13}OClO_3$	58
$HOCH_2CH_2OH$	$O_3ClOCH_2OClO_3$	60
$HOCH_2(CH_2)_2CH_2OH$	$O_3ClOCH_2(CH_2)_2CH_2OClO_3$	38
CF_3CH_2OH	$CF_3CH_2OClO_3$	55
$CH_3C(NO_2)_2CH_2OH$	$CH_3C(NO_2)_2CH_2OClO_3$	67
$FC(NO_2)_2CH_2OH$	$FC(NO_2)_2CH_2OClO_3$	60
$FC(NO_2)_2CH_2OCH_2CH_2OH$	$FC(NO_2)_2CH_2OCH_2CH_2OClO_3$	43
$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2OClO_3$	48
$HC{\equiv}CCH_2OH$	$HC{\equiv}CCH_2OClO_3$	43
$CH_3CHOHCH_3$	$CH_3CH(OClO_3)CH_3$	48
$CH_3CHOH(CH_2)_3CH_3$	$CH_3CH(OClO_3)(CH_2)_3CH_3$	62
$CH_3CH_2CHOH(CH_2)_2CH_3$	$CH_3CH_2CH(OClO_3)(CH_2)_2CH_3$	53

Alcohols can serve as the starting materials in the synthesis of covalent perchlorates in yet another reaction, which is a deoxygenation process. In this reaction, developed by the authors of the present review,[43] sulphur, chlorine, pyridine, and lithium perchlorate were used as the reagents. The possibility of the formation of covalent perchlorates is because the alcohols are intially converted into chlorosulphenates by the sulphur dichloride arising as an intermediate and these then generate dichloroalkoxysulphonium ions, which undergo nucleophilic substitution by the perchlorate anion:

$$ROH \xrightarrow[SCl_2]{S+Cl_2} [ROSCl] \xrightarrow{Cl_2} [ROSCl_2^+Cl^-] \xrightarrow{ClO_4^-} ROClO_3,$$

$R = C_8H_{17}$, 2-chlorocyclohexyl.

The reactions of ethers with chlorine heptoxide and acyl perchlorates have been investigated.[54] Acyl perchlorates, obtained by the reaction of acyl chlorides with silver perchlorates (see below) in carbon tetrachloride, cleave secondary ethers with formation of a mixture of secondary alkyl perchlorates and alkyl acetates:

$$(CH_3)_2CHOCH(CH_3)_2 + CH_3\overset{\overset{O}{\|}}{C}OClO_3 \rightarrow (CH_3)_2CHOClO_3 + (CH_3)_2CHOCOCH_3.$$

Primary ethers do not enter into this reaction. Like acetyl perchlorate, benzoyl and *NN*-diethylcarbamoyl perchlorates react with ethers.[54]

In contrast to acyl perchlorates, chlorine heptoxide is capable of cleaving not only secondary but also primary ethers.[54] For example, diethyl ether reacts slowly with chlorine heptoxide, forming ethyl perchlorate.[54]

The main product of the reaction of diisopropyl ether with chlorine heptoxide is the geminal diperchlorate (I),[54] which can also be obtained by the reaction of acetone with chlorine heptoxide[55] or with anhydrous perchloric acid:[56]

$$(CH_3)_2CHOCH(CH_3)_2 + Cl_2O_7 \longrightarrow \left.\begin{array}{l} \\ \\ CH_3\overset{\overset{O}{\|}}{C}CH_3 + 2HClO_4\ (\text{or } Cl_2O_7) \end{array}\right\} \rightarrow CH_3\overset{\overset{OClO_3}{|}}{\underset{\underset{OClO_3}{|}}{C}}CH_3 \quad (I)$$

Esters can apparently also be cleaved by chlorine heptoxide with formation of covalent perchlorates. A single reaction of this type, resulting in the formation of ethyl perchlorate, has been described in the literature[57] (in relation to ethyl carbamate):

$$3NH_2\overset{\overset{O}{\|}}{C}OC_2H_5 + Cl_2O_7 \rightarrow C_2H_5OClO_3 + [H_2NC(OH)OC_2H_5]^+ClO_4^- + H_2N\overset{\overset{O}{\|}}{C}NH\overset{\overset{O}{\|}}{C}OC_2H_5.$$

Cyclic ethers, including epoxides, can also be used as the starting compounds for the synthesis of organic perchlorates. It has been suggested that[54] they be cleaved with acyl perchlorates and chlorine heptoxide. For example, the reactions of acetyl perchlorate with tetrahydrofuran and epoxyethane take place at 0 °C with formation of the corresponding αω-acetoxyperchlorates:

$$\underset{n=2,4}{\overset{(CH_2)_n}{\underset{O}{\bigcirc}}} + CH_3\overset{\overset{O}{\|}}{C}OClO_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}O(CH_2)_nOClO_3 \quad (78\text{–}89\%).$$

Analogous reactions with chlorine heptoxide[47] lead to αω-diperchlorates:

$$\bigcirc\!\!\!\!\!O + Cl_2O_7 \rightarrow O_3ClO(CH_2)_4OClO_3, \quad 83\%$$

$$\bigcirc\!\!\!\!\!O + Cl_2O_7 \rightarrow O_3ClO(CH_2)_3OClO_3, \quad 55\%$$

$$CH_3\text{—}\underset{\diagdown O \diagup}{CH}\text{—}CH\text{—}CH_3 + Cl_2O_7 \rightarrow CH_3\text{—}\underset{O_3ClO}{CH}\text{—}\underset{OClO_3}{CH}\text{—}CH_3 \quad 30\%.$$

Acid cleavage of epoxides can also be used for the synthesis of covalent perchlorates. As early as the beginning of the XXth century, Hofmann et al.[58] investigated the reactions of epoxyethane and epichlorohydrin with concentrated (70%) perchloric acid and obtained the explosive compounds (II) and (III):

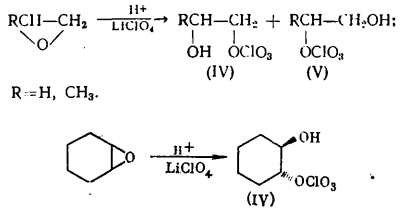
$$2CH_2\text{—}\underset{\diagdown O \diagup}{CH_2} + HClO_4 \rightarrow \underset{\underset{OH}{|}}{CH_2}\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH_2OClO_3, \quad (II)$$

$$CH_2\text{—}\underset{\diagdown O \diagup}{CH}CH_2Cl + HClO_4 \rightarrow CH_2\text{—}\underset{\underset{OClO_3}{|}}{\overset{\overset{OH}{|}}{CH}}\text{—}CH_2Cl. \quad (III)$$

The kinetics of the opening of the epoxide rings with perchloric acid[59] or other acids in the presence of lithium perchlorate[60] have been investigated in detail. Strong evidence has been obtained in support of the carbonium ion character of the intermediates in these

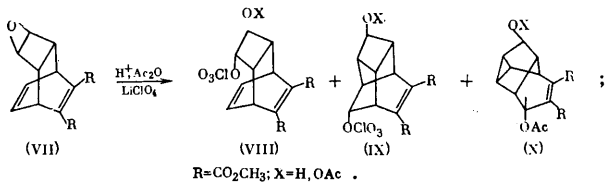
processes,[59] but the formation of covalent perchlorates was not detected in the above studies.[59,60]

The authors of the present review developed a preparative method for the synthesis of covalent perchlorates in reactions involving coupled acid opening of epoxide rings in the presence of perchloric acid salts.[37,40] Epoxyethane, epoxypropane, epoxycyclohexane, and also the epoxy-derivative (VII) of tricyclo[4.2.2.0^{2,5}]decane were chosen as the objects of study. Covalent perchlorates were obtained in all cases by treating these compounds with an acid (acetic, sulphuric, or perchloric) in the presence of lithium perchlorate in ether or ethyl acetate. The β-hydroxy-perchlorates (IV)–(VI) are formed under these conditions from the epoxy-derivatives obtained from alkenes and cyclohexene:[37,40]



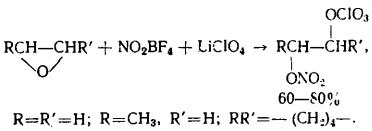
R=H, CH_3.

The acid cleavage of the skeletal epoxide (VII) in the presence of lithium perchlorate resulted in the formation of a complex mixture of products including the covalent perchlorates (VIII) and (IX):[38,39]



R=CO_2CH_3; X=H, OAc .

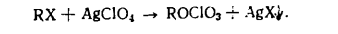
When the epoxide rings are opened not with an acid but with nitronium fluoroborate in the presence of lithium perchlorate in an inert solvent, the formation of β-nitratoalkyl perchlorate in high yields is observed:[37]



R=R′=H; R=CH_3, R′=H; RR′=—$(CH_2)_4$—.

3. Synthesis From Alkyl Halides

During recent years, the method of synthesis of alkyl perchlorates by the exchange reaction of alkyl halides with silver perchlorate in an organic solvent has come to be most widely used:



Anhydrous silver perchlorate is readily soluble in many organic solvents (the solubility of $AgClO_4$ in 100 g of the solvent is 5.3 g in benzene and 101 g in toluene[1]); when an equivalent amount of an alkyl halide is added to such a solution, the rapid formation of a silver halide precipitate is observed, and its rapid removal can produce a solution containing only the alkyl perchlorate. Dilute solutions of alkyl perchlorates are usually safe to handle.

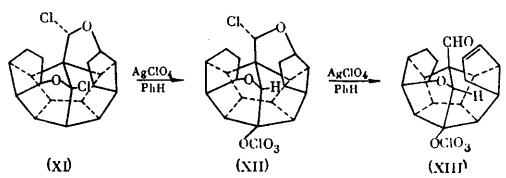
The reactions of alkyl halides with silver perchlorate in a wide variety of solvents have been investigated. It has been shown that ethanol,[24] acetonitrile,[61] and anisole[62] are relatively unsuitable for the synthesis of alkyl perchlorates, which are excellent alkylating agents[4] and readily react with these solvents. The use of chlorohydrocarbon solvents, for example, carbon tetrachloride, which may react with silver perchlorate to form the explosive trichloromethyl perchlorate,[63] is not recommended either. In practice, diethyl ether,[23] dioxan,[64] nitromethane,[65,66] pentane,[67] and benzene[68] are used for the preparative synthesis of alkyl perchlorates.

Alkyl perchlorates are usually obtained from alkyl iodides,[6,67,69,70] although the reactions of alkyl bromides with silver perchlorate have also been studied.[23,68] A series of n-alkyl perchlorates have been prepared by the reaction of C_5–C_8 alkyl iodides with silver perchlorate in pentane in 90–95% yields.[67] However, recent studies[6,51] have cast doubt on the result of this reaction. It was found that, when the reaction of alkyl iodides is carried out in the majority of solvents, with the exception of benzene, a mixture of primary and secondary perchlorates is formed:

For example, this reaction in carbon tetrachloride affords a 1:1 mixture of primary and secondary perchlorates;[6] on the other hand, the reaction of primary alkyl iodides with silver perchlorate in benzene gives a 90% yield of primary alkyl perchlorates exclusively.[6]

The reaction of halogeno-derivatives with silver perchlorate has also uses other than the synthesis of alkyl perchlorates. It has been shown by indirect chemical methods[69,71] and also by ^{1}H NMR [51] that allyl and benzyl perchlorates, as well as acyl perchlorates,[54] can be obtained analogously from acyl chlorides and silver perchlorate:

Covalent silyl perchlorates[72,73] and certain skeletal perchlorates of the norbornane[74] and adamantane[19,20] series have been synthesised by the reactions of the corresponding halides with silver perchlorate. The skeletal covalent perchlorates (XII) and (XIII) have been synthesised by treating the dichloride (XI) (heterocyclic analogue of trisecododecahedrane) with silver perchlorate in benzene:[16,17]



It has been noted[16] that compound (XIII) is the first example of a stable tertiary covalent perchlorate.

The mechanism of the reaction of alkyl halides with silver perchlorate has been investigated quite vigorously. As early as 1940, the kinetics of the reaction of methyl iodide with silver perchlorate were studied in acetic acid, acetone, ethanol, benzene, ethyl acetate, and 50% aqueous ethanol.[70] It was found that the order of this reaction depends on the initial concentration of the reactants and is on average 2.5; the activation energy is 11–13 kcal. The authors[70] established that the rate of reaction is influenced by the excess colloidal silver iodide, which is not removed from the solution for a long time. Further studies[65,66,68,75] showed that the reaction of alkyl iodides with silver perchlorates proceeds via the formation of the ion-pair complex (XIV), which slowly decomposes in a solvent

with a low dielectric constant to a covalent perchlorate and silver halide:

$$RX + AgClO_4 \rightleftarrows [ClO_4^-R^+X^-Ag^+] \rightarrow \text{products.}$$
(XIV)

The reaction of 2-octyl bromide with silver perchlorate in nucleophilic (acetonitrile)[61] and non-nucleophilic (benzene)[68] solvents has been investigated. In both solvents, the reaction is of first order with respect to alkyl bromide and of variable order with respect to silver perchlorate. In acetonitrile, the reaction order with respect to silver perchlorate varies from 1 (at very low concentrations of the salt) to 2 (for 0.3 M $AgClO_4$); in benzene, the order with respect to silver perchlorate varies from 1.5 to 2. These results are consistent with earlier data.[70] It has also been observed[61,68] that, at low silver perchlorate concentrations, small amounts of added tetrabutylammonium perchlorate have a considerable catalytic effect; furthermore, the formation of olefins as side products is reduced in the presence of the ionic perchlorate. The catalytic action of the salt has been explained[61] by the nucleophilic involvement of the perchlorate anion in the rate-limiting stage of the reaction. The reaction with the optically active 2-octyl bromide in benzene leads to the formation of a 2:3 mixture of the enantiomeric 2-octyl perchlorates, the product with the inverted configuration predominating.[68] This result is independent of the silver perchlorate concentration and the addition of tetrabutylammonium perchlorate. It has been noted[68] that the reaction of 2-octyl bromide with silver perchlorate in benzene is much faster than in acetonitrile as a consequence of the formation of a strong complex between the Ag^+ cation and acetonitrile.

Since the ion-pair association and the tendency towards the formation of ionic aggregates by silver perchlorate greatly complicate the study of the kinetics of the reactions with alkyl halides in benzene, a solvent with a high dielectric constant (nitromethane), in which silver perchlorate is almost wholly ionised, was used.[65,66] The reaction of methyl iodide with silver perchlorate in nitromethane takes place with formation of 80% of methyl perchlorate and 20% of a side product of unknown composition, which precipitates together with silver iodide as a red amorphous deposit.[66] As for the other solvents, the complex (XIV) is formed in the first stage of the process and then decomposes rapidly, in several stages, into the final reaction products. The same mechanism has been proposed[65] for the reaction of neopentyl iodide with silver perchlorate in nitromethane, but the rate of this reaction is 33 times greater than that of the analogous reaction of methyl iodide.

The reaction of alkyl halides with silver perchlorate has found a practical application, mainly for the synthesis of methyl perchlorate, which is a powerful methylating agent.[76–78] A disadvantage of this method of synthesis of covalent perchlorates is the necessity to use the expensive and explosive anhydrous silver perchlorate.[1] The possibility of a rearrangement when primary alkyl iodides are used also diminishes the synthetic value of the reaction.[6]

The methods of synthesis of covalent perchlorates from alkyl iodides based on the oxidative iodine elimination reactions are partly free from these disadvantages. The central feature of these processes consists in the oxidation of the iodine atom in alkyl iodides to the tervalent state by various reagents (halogens,[79–81] peracids,[82] and a wide range of inorganic oxidants[83–85]) with formation of intermediates of type (XV). The iodine atom in the +3 oxidation state exhibits the properties of an exceptionally effective leaving group and can be readily substituted by the nucleophiles present,[79,82] including perchlorate anions:[36,44,45,86,87]

$$\text{>C–I} \xrightarrow{\text{oxidant}} \left[\text{>C–I<}\right] \xrightarrow{ClO_4^-} O_3ClO\text{–C<}.$$
(XV)

Inorganic reagents can be represented in this reaction by a pair of substances, namely the oxidant–perchlorate anion-donor pair,[36,44,45] or by a single substance such as chlorine heptoxide,[87] a halogen perchlorate,[12,86,77] or μ-oxodiiodosodiphenyl diperchlorate.[89]

Chlorine[90] and bromine[91] perchlorates have been used[12,86,88] to synthesise perfluorinated alkyl perchlorates. These reagents were first obtained at the beginning of the 1970s in 70–95% yield by keeping caesium perchlorate or nitronium perchlorate with the fluorosulphate of the corresponding halogen for a long time at –45 °C:[90,91]

$$MClO_4 + XSO_3F \rightarrow MSO_3F + XOClO_3,$$
$$M{=}Cs,\ NO_2;\ X{=}Cl,\ Br.$$

The reactions of lower perfluorinated alkyl iodides with chlorine perchlorate take place smoothly at temperatures between –200° and –45 °C with formation of stable covalent perfluoroalkyl perchlorates (XVII) in 95–99% yield:[12,86,88]

$$C_nF_{2n+1}I + 2ClOClO_3 \xrightarrow[-Cl_2]{} \underset{\text{(XVI)}}{C_nF_{2n+1}I(ClO_4)_2} \rightarrow \underset{\text{(XVII)}}{C_nF_{2n+1}OClO_3} + [IClO_4].$$

Compound (XVI), formed in the first stage of the reaction of trifluoromethyl iodide or pentafluoroethyl iodide with fluorine perchlorate, cannot be isolated and the final products of the reaction are gaseous perfluoroalkyl perchlorates, chlorine, and the products of the decomposition of the unstable iodine perchlorate. However, in other cases it is possible to obtain crystalline intermediates stable at room temperature, for example, $(CF_3)_2CFI(ClO_4)_2$ (m.p. 71 to 73 °C) and $C_7F_{15}I(ClO_4)_2$ (m.p. 56–78 °C), which decompose on moderate heating (below 100 °C) with formation of the corresponding covalent perchlorate.[12]

Bromine perchlorate reacts analogously with perfluoroalkyl iodide, but the yields of perfluoroalkyl perchlorates are somewhat lower in this case.[12] The replacement of perfluoroalkyl iodides by the bromides also entails a decrease in the yields of covalent perchlorates. The most stable halogen perchlorate, namely fluorine perchlorate, gives rise to only trace amounts of covalent perchlorates in its reaction with perfluoroalkyl iodides.[13] We may note that halogen perchlorates are extremely explosive even at temperatures of about –200 °C and rapidly decompose at room temperature.[90,91]

The studies of Schack and co-workers[86,88] stimulated the investigation of the reactions of alkyl iodides with chlorine heptoxide. Thus it has been found[87] that the main products of these reactions are covalent perchlorates and the formation of the intermediate (XVIII) with tervalent iodine was postulated:

$$R{-}I + Cl_2O_7 \rightarrow \underset{\text{(XVIII)}}{\left[R{-}I\begin{matrix}ClO_3\\OClO_3\end{matrix}\right]} \rightarrow ROClO_3 + \underset{\text{(XIX)}}{[IClO_3]}.$$

The unstable iodine chlorate (XIX) formed decomposes with formation of I_2O_5 and Cl_2O. The presence of halogen oxides and mixed iodine and chlorine oxides in the reaction mixture leads to the formation of esters and ethers as side products. For example, 22% of ethyl acetate and trace amounts of diethyl ether are obtained together with ethyl perchlorate (63%) in the reaction of ethyl iodide with an excess of chlorine heptoxide at 0 °C:

$$C_2H_5I + Cl_2O_7 \rightarrow I_2O_5 + C_2H_5OClO_3 + CH_3\underset{\underset{O}{\|}}{C}OC_2H_5 + C_2H_5OC_2H_5.$$

The use of an equivalent amount of chlorine heptoxide lowers the yield of ethyl perchlorate and leads to a sharp increase in the content of diethylether in the reaction mixture (more than 20%).

In the course of the study of the phenomenon of the competitive binding of ultraweak nucleophiles in carbonium ion processes, the present authors investigated the possibility of the formation of covalent perchlorates in the oxidative decomposition of alkyl iodides.[44,45,89] The methods of synthesis of alkyl perchlorates developed are based on the oxidation of alkyl iodides in the presence of perchloric acid salts which in this case play the role of a reagent—a source of perchlorate anions:

$$CH_3(CH_2)_nI + M^+ClO_4^- \xrightarrow{[Ox]} CH_2(CH_2)_nOClO_3,$$
$$n = 0-5;\ M = Li,\ Bu_4N;\ [Ox] = m\text{-}ClC_6H_4COOOH,\ H_5IO_6,\ Cl_2,\ NO_2BF_4.$$

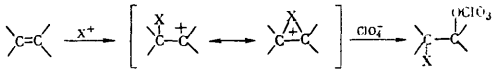
The reactions were performed by adding an oxidant [Ox], for example, chlorine, *m*-chloroperbenzoic acid, or iodic acid, to a solution of alkyl iodide in an aprotic solvent (ether, ethyl acetate, or chloroform) in the presence of 1–5 equivalents of lithium perchlorate or tetrabutylammonium perchlorate. Alkyl perchlorates were isolated in 50–70% yield by distillation or chromatography on a silica gel column. The geminal methylene diperchlorate (XX) was obtained for the first time by the oxidative deiodination of methylene iodide:[45]

$$CH_2I_2 + 2LiClO_4 + 2NO_2BF_4 \rightarrow \underset{(XX)}{CH_2(OClO_3)_2}.$$

The oxidation of organic iodides in the presence of sources of perchlorate anions is in our view one of the safest and most convenient methods of synthesis of covalent perchlorates of different types.

4. Synthesis From Olefins

The possibility of obtaining covalent perchlorates from olefins is associated with a two-stage mechanism of the electrophilic addition and generation of carbonium ion intermediates:



The addition of perchloric acid, chlorine heptoxide, and halogen perchlorate has been studied in special detail.[13,50,55,92–95] The studies of the reaction of but-2-ene with anhydrous perchloric acid in methylene chloride were some of the first in this field.[92] The organic perchlorate could not be isolated from the reaction mixture after treatment with water, but identification of 2-butanol and diisobutyl ether confirmed indirectly the formation of 2-butyl perchlorate in this reaction. The authors[92] also reported powerful explosions, which occurred when the butene was introduced into the perchloric acid solution.

The study of the reaction of *cis*-octadec-9-ene with 70% perchloric acid at 100 °C showed[93] that rapid migration of the double bond in the molecule is observed under these conditions. Octadecyl esters of perchloric acid are formed in the above reaction only in trace amounts (2%), while an olefin with a terminal double bond affords 14% of the perchlorate under the same conditions. The reaction of unsubstituted olefins with perchloric acid in the presence of oleum and an inert organic solvent (hexane, chlorobenzenes, etc.) has been studied in greater detail.[50,94] Higher yields of perchlorate (up to 100%) were obtained at reduced temperatuers (–10 °C); the increase to room temperature leads to a sharp reduction of the yields.[50]

Table 2. The yields of secondary alkyl perchlorates in the reactions of olefins with perchloric acid in the presence of a acid catalyst (H_2SO_4 + SO_3).[50]

Olefin	Reaction product	Yield, %
Propene	$CH_3CH(OClO_3)CH_3$	96
Pent-1-ene	$CH_3CH(OClO_3)(CH_2)_2CH_3$	98
Hex-1-ene	$CH_3CH(OClO_3)(CH_2)_3CH_3$	99
Cyclohexene	$(CH_2)_5CHOClO_3$	89
Dec-1-ene	$CH_3CH(OClO_3)(CH_2)_7CH_3$	100
Octadec-1-ene	$CH_3CH(OClO_3)(CH_2)_{15}CH_3$	100
4-Phenylbut-1-ene	$PhCH_2CH_2CH(OClO_3)CH_3$	85
5-Methylhex-1-ene	$CH_3CH(CH_3)CH_2CH_2CH(OClO_3)CH_3$	76
Octa-1,7-diene	$CH_3CH(OClO_3)(CH_2)_4CH(OClO_3)CH_3$	85

In a study of the reactions of olefins with chlorine heptoxide in carbon tetrachloride, it was shown that they usually proceed with formation of a mixture of perchlorates, whose composition is determined by the structure of the olefin.[55] Thus the reaction of propene with chlorine heptoxide affords a mixture of 2-propyl and 1-chloropropyl perchlorates:

$$CH_2{=}CHCH_3 + Cl_2O_7 \rightarrow \underset{\substack{|\\OClO_3\\32\%}}{CH_3CHCH_3} + \underset{\substack{|\\OClO_3\\17\%}}{ClCH_2CHCH_3}.$$

Under these conditions, but-2-ene gives rise to the more complex mixture of products (XXI)–(XXIII), which is the same for the *cis*- and *trans*-olefins:

$$CH_3CH{=}CHCH_3 + Cl_2O_7 \rightarrow \underset{\substack{|\\OClO_3\\(XXI)}}{CH_3CH(OClO_3){-}CHCH_3} + \underset{\substack{|\\Cl\\(XXII)}}{CH_3CH(OClO_3){-}CHCH_3} + \underset{\substack{\|\\O\\|\\OClO_3\\(XXIII)}}{CH_3CCHCH_3}.$$

The reaction of tetramethylethylene with chlorine heptoxide leads to the formation of a mixture of the geminal diperchlorates (I) and (XXIV), which are insoluble in carbon tetrachloride:

$$\underset{\substack{CH_3\quad CH_3\\ \diagdown\ \diagup\\ C{=}C\\ \diagup\ \diagdown\\ CH_3\quad CH_3}}{} + Cl_2O_7 \rightarrow \underset{\substack{|\\OClO_3\\(I)}}{CH_3{-}C(OClO_3){-}CH_3} + \underset{\substack{|\\OClO_3\\(XXIV)}}{CH_3{-}C(OClO_3){-}C(CH_3)_3}.$$

Olefins with electron-accepting substituents (1,1-difluoroethylene, allyl chloride) and ethylene virtually do not react with chlorine heptoxide, but the addition of small amounts of water catalyses the reaction and leads to acceptable yields of perchlorates, which are in this case the products of the addition of perchloric acid to the double bond:

$$CF_2{=}CH_2 + Cl_2O_7 \xrightarrow[CCl_4]{H_2O} \underset{76\%}{CH_3CF_2OClO_3},$$

The wide variety of products in the reactions of olefins with chlorine heptoxide is apparently due to the combination of oxidation-reduction processes and a series of secondary reactions.[55] For example, the formation of the diperchlorate (XXI) can be explained by the interaction of chlorine heptoxide with the epoxide formed when but-2-ene is oxidised.

The additon of halogen perchlorates to the double bond has been studied in relation to perfluorinated olefins.[13,95] The reactions of chlorine and bromine perchlorates with tetrafluoroethylene, perfluoropropene, chlorotrifluoroethylene, and other perhalogeno-olefins take place rapidly at temperatures below -70 °C and lead to perhalogenoalkyl perchlorates in high yields (90–100%).[95] Chlorine and bromine perchlorates add to perfluoropropene strictly regiospecifically with formation of products of only kind—the perchlorates (XXV), in accordance with the Markovnikov rule, which is strong evidence in support of a polar addition mechanism:

$$CF_3CF{=}CF_2 + XOClO_3 \rightarrow CF_3CFXCF_2OClO_3. \quad (XXV)$$

X=Cl, Br.

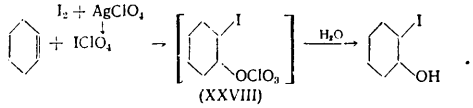
On the other hand, a mixture of isomers having the normal structure [compound (XXVI)] and the iso-structure [compound (XXVII)] is formed in the reaction of fluorine perchlorate with perfluoropropene:[13]

$$CF_3CF{=}CF_2 + FOClO_3 \rightarrow CF_3CF_2CF_2OClO_3 + CF_3\underset{\underset{OClO_3}{|}}{C}FCF_3.$$

(XXVI), 68% (XXVII), 32%

For this reaction, the authors[13] also proposed an ionic addition mechanism; the formation of the secondary perchlorate (XXVII) can be accounted for by the initial electrophilic attack by the oxygen atom on the carbon atom in the 2-position (the polarity of the F–O bond is probably the opposite of that of the Cl–O and Br–O bonds).

The addition of halogen perchlorates to unsaturated hydrocarbons has not been investigated. The only study on these lines[96] is at present only of historical interest. The authors[96] suggested that an ethereal solution of silver perchlorate and iodine contains iodine perchlorate and attempted to obtain 2-iodocyclohexyl perchlorate by treating cyclohexene with this solution:



(XXVIII)

However, the reaction product (XXVIII) proved to be unstable and the authors were able to isolate only 2-iodocyclohexanol after treating the reaction mixture with water. Here we may note that, according to the latest data,[12,97] iodine perchlorate is unstable and decomposes with formation of compounds of iodine in higher oxidation states even at temperatures below -50 °C. We therefore think that the explanation of the formation of compound (XXVIII) by the addition of ClO_4 to cyclohexene[96] is unlikely. An alternative mechanism may involve the coupled addition of iodine and the perchlorate anion to the double bond (see below).

In the course of a study of the competitive binding of the perchlorate anion in carbonium ion processes, we studied in detail the reactions involving the coupled electrophilic addition of perchlorate to olefins.[14,15,35,98–100] A whole series of such reactions can be used for the preparative synthesis of covalent perchlorates. For example, the reactions of unsubstituted olefins (ethylene, hept-1-ene, and cyclohexene) with halogens or nitronium fluoroborate in the presence of a (2–10)-fold excess of lithium perchlorate take place smoothly in an aprotic organic solvent (ether, ethyl acetate, methylene chloride) with formation of β-halogeno- or β-nitro-perchlorates.[35] The addition takes place in accordance with the Markovnikov rule:

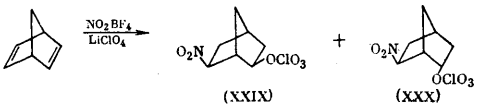
$$RCH{=}CHR' + XY + LiClO_4 \rightarrow RCH(X){-}CHR'(OClO_3),$$

30–70%

R=R'=H; R=C_6H_{11}, R'=H;
RR'=$(CH_2)_4$; XY=Cl_2, Br_2, NO_2BF_4.

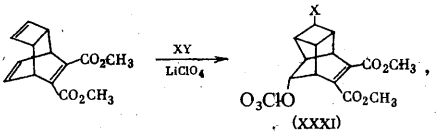
The reaction with cyclohexene leads to a mixture of the *cis*- and *trans*-substituted perchlorates.

The electrophilic perchlorate addition reactions have been investigated also for a series of skeletal olefins.[14,15,35] Thus norbornadiene reacts with nitronium fluoroborate and lithium perchlorate in ethyl acetate to form a mixture of the isomeric nitroperchlorates (XXIX) and (XXX) of the nortricyclene series (overall yield 72%):

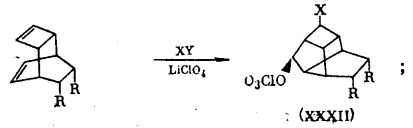


(XXIX) (XXX)

The reactions of skeletal olefins of the tricyclo[4.2.2.$0^{2,5}$]decane series with electrophiles and lithium perchlorate afford, together with other rearranged products, stable skeletal perchlorates,[14,15] for example:



(XXXI)



(XXXII)

R=CH_3,CO_2CH_3.

The yields of the skeletal perchlorates (XXXI) and (XXXII) in these reactions reach 80%.

5. Synthesis of Covalent Perchlorates by Fragmentation Reactions

The next group of methods of synthesis of covalent perchlorates combines reactions involving the elimination of an electrically neutral species (N_2, CO_2, etc.) in the first stage. The reaction of alkyl chloroformates with silver perchlorate in benzene can be included among reactions of this type.[101] This reaction proceeds via a stage involving the elimination of a CO_2 molecule and leads to alkyl perchlorates together with benzene alkylation side products. In the course of the reaction, primary alkyl derivatives isomerise to secondary alkyl derivatives. The authors[101] proposed the following reaction mechanism:

$$ROCOCl \xrightarrow{Ag^+} \left[ROC^+(=O)\right] \xrightarrow{-CO_2} [R^+] \begin{cases} \xrightarrow{ClO_4^-} ROClO_3 + R'OClO_3, \\ \xrightarrow{-H^+} \text{alkene} + HClO_4 \rightarrow \text{polymer}, \\ \xrightarrow{C_6H_6} RC_6H_5 + R'C_6H_5, \end{cases}$$

where R is a primary alkyl and R' a secondary alkyl.

The yields of the perchlorates and benzene alkylation products in the reaction of chloroformate with a solution of silver perchlorate in benzene at 25 °C are given in Table 3. We may note that the low selectivity of this reaction limits significantly the scope of its use.

Table 3. The yields (%) of the products of the reactions of alkyl formates (ROCOCl) with silver perchlorate in benzene at 25 °C.[101]

R	$ROClO_3$	RC_6H_5	$R'OClO_3$	$R'C_6H_5$
CH_3	86	14	—	—
C_2H_5	47	37	—	—
n-C_3H_7	—	—	70*	10*
iso-C_3H_7	70	10	—	—
iso-C_4H_9	—	—	—	37**

*R′ = iso-C_3H_7; **R′ = t-C_4H_9.

The recently proposed[102,103] method of preparative nucleophilic substitution via "betylates"—salt-like compounds which are capable of readily eliminating the betaine fragment with formation of a covalent nucleophilic substitution product—is of undoubted synthetic value. In particular, the synthesis in 100% yield of 1-hexadecyl perchlorate via the betylate (XXXIII) by heating in toluene has been described:[102,103]

$$ROH \rightarrow ROSO_2(CH_2)_2\overset{+}{N}(CH_3)_3\,ClO_4^- \rightarrow ROClO_3 + {}^-O_3S(CH_2)_2\overset{+}{N}(CH_3)_3,$$
(XXXIII)

R=$C_{16}H_{33}$.

The reactions of aliphatic diazo-compounds with perchloric acid are accompanied by the evolution of nitrogen and also usually lead to covalent perchlorates. A reaction of this type was first carried out in a study[23] where methyl perchlorate was obtained by treating a solution of perchloric acid in ether with diazomethane:

$$CH_2N_2 + HClO_4 \rightarrow CH_3OClO_3 + N_2.$$

The authors[23] noted an extremely high risk of explosion in this method of synthesis of methyl perchlorate.

Dutch workers[11,104] used the reaction of diazosulphones with 70% perchloric acid in dichloroethane to synthesise covalent arenesulphonylmethyl perchlorates (XXXIV), whose yields reached 50%:

$$ArSO_2CHN_2 + HClO_4 \leftarrow ArSO_2CH_2OClO_3 + N_2,$$
(XXXIV)

Ar = p-$CH_3C_6H_4$, $C_6H_5CH_2$, C_6H_5, p-ClC_6H_4, m-ClC_6H_4, p-$NO_2C_6H_4$.

The present authors[36,105] investigated the deamination of alkylamines with nitrous acid in the presence of lithium perchlorate. These processes, which also proceed via the intermediate formation of diazoalkanes, lead to covalent perchlorates as a result of the nucleophilic substitution of the diazo-group by the perchlorate anion. The reactions were carried out by adding various acids (for example, acetic or hydrochloric) to a mixture of alkylamines, sodium nitrite, and lithium perchlorate in an organic solvent (ether, ethyl acetate) or in water:

$$RNH_2 + NaNO_2 + HX + LiClO_4 \rightarrow ROClO_3,$$
R = n-C_4H_9, n-C_7H_{15}, n-C_9H_{19}; X = Cl, OAc.

Alkyl perchlorates were isolated from the reaction mixture in 30–40% yields.

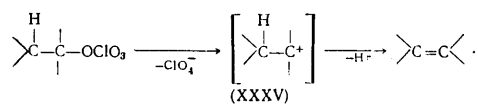
In conclusion of this Section, we emphasise yet again that all the traditional methods of synthesis of covalent perchlorates involve the risk of explosion to a greater or lesser extent. This risk is largely due to the nature of the inorganic reagents themselves—donors of the perchlorate group. Anhydrous silver perchlorate, which is most often used for this purpose, explodes even on friction.[1] The extremely high danger of the explosion of perchloric acid and chlorine heptoxide, especially on contact with organic solvents, is generally known. Fluorine, chlorine, and bromine perchlorates are unstable and extremely explosive at any temperatures and in any state.[90,91] On the other hand, the methods of synthesis of covalent perchlorates developed by the present authors[14,15,34,48,89,98–100] are more acceptable for practical use, since the reagents in these reactions are the lithium or alkylammonium salts of perchloric acid, which are safe to handle.

III. PROPERTIES

1. Physicochemical Properties and the Problem of Stability

A common property, characteristic of virtually all covalent organic perchlorates is a high risk of their explosion. The first investigators,[2,23] who obtained the simplest alkyl perchlorates, already noted that these highly volatile liquids (the boiling points of ethyl and methyl perchlorates are respectively 52° and 89 °C [23]) are very dangerous to handle. The perchlorates of monohydric alcohols[1,49] and also the lowest β-nitroalkyl[35] and β-nitratoalkyl[37] perchlorates are even more dangerous—these compounds are explosive even in solutions!

Furthermore, a very low thermal stability has been noted for many organic perchlorates: even at room temperature, these compounds char rapidly or polymerise. The low stability of covalent perchlorates is apparently due to the highly nucleofugitive nature of the perchloryloxy-group, i.e. the ease with which it can be expelled from the carbon skeleton with formation of carbonium ion intermediates (XXXV) and elimination products:



(XXXV)

The subsequent interaction of these species with one another leads to polymeric products. Evidently, perchlorates containing substituents capable of stabilising the carbonium ion (XXXV) formed and hence facilitating the heterolytic dissociation of the C–$OClO_3$ bond, will be the least stable. Indeed, according to the available literature data, t-alkyl perchlorates,[51,62] allyl perchlorates,[71] and benzyl perchlorates[106,107] are the least stable; when an attempt is made to obtain them by treating the corresponding halogeno-derivative with silver perchlorate in nitromethane, the mixture chars or a polymeric deposit is formed (molecular weight about 1000 [106,107]).

On the other hand, the presence of electron-accepting substituents in the molecule hinders the heterolysis of the C–$OClO_3$ bond, which usually increases the stability of the perchlorates. Thus perfluoroalkyl perchlorates can be stored at room temperature for years,[12,86]

decomposing only slowly on heating to 200 °C, and are hardly hydrolysed by water. Trifluoromethyl perchlorate decomposes slowly on heating above 100 °C only in the presence of a catalyst—caesium fluoride:[12,88]

$$CF_3OClO_3 \xrightarrow{CsF} COF_2 + FClO_3.$$

The polyperchlorates of polyhydric alcohols[1] and *gem*-diperchlorates[56] are apparently more stable on heating than alkyl perchlorates. 2,2-Diperchloryloxypropane (I), obtained by Baum,[56] can be distilled without decomposition and explodes only on heating to 250 °C; however, *gem*-diperchlorates are exceptionally sensitive to the action of water.

Arenesulphonylmethyl perchlorates (XXXIV) have a high thermal stability.[11,104] These compounds melt without decomposition at temperatures above 100 °C but are extremely explosive.[11] It has been reported[108] that explosions of the single crystals in the diffractometer were observed during the X-ray diffraction analysis of toluene-*p*-sulphonylmethyl perchlorate.

It is interesting to note for comparison that covalent silyl perchlorates exhibit a higher stability than alkyl perchlorates.[18,72,73,109,110] Trialkylsilyl perchlorates $R_3SiOClO_3$ (R = CH_3, C_2H_5, n-C_3H_7, or t-C_4H_9) are oily liquids which fume in air and can be purified by vacuum distillation. The reaction of t-butyl dimethylsilyl perchlorates with alcohols can be used to introduce the trialkylsilyl protecting group.[18,110]

Skeletal perchlorates with a rigid carbon skeleton are more stable than alkyl perchlorates. The stable skeletal perchlorates (XIII), in which the perchlorate group is attached to a tertiary carbon atom, has been obtained.[16,17] Skeletal covalent secondary perchlorates, obtained by the present authors,[15] melt without decomposition at 120—150 °C, are insensitive to impact, and can be stored at room temperature for a long time without appreciable decomposition.

2. Identification

The problem of the identification of perchloric acid ester arose in the first studies on the synthesis of these compounds.[23,24,58] The highly explosive nature of covalent perchlorates precluded elemental analysis by combusting the specimen and hindered the use of chemical identification methods. The explosive decomposition of the lower perchlorates on heating in a capillary was used as a qualitative test for perchlorates.[68] The first quantitative methods for the determination of perchloric acid esters consisted in treating the specimen with an alcoholic solution of KOH with subsequent gravimetric determination of the precipitate of potassium perchlorate, which is insoluble in ethanol.[25] A more modern modification of this method consists in the titrimetric determination of the amount of alkali needed for the complete hydrolysis of the perchloric acid ester.[19,49] It has been found[62,69,71,102,103,111] that covalent perchlorates readily alkylate anisole and toluene in the *para*-position. In its analytical version, this reaction can also be used for the identification of perchlorates. The hydrolysis to alcohols with a known structure has likewise been employed to identify certain perchloric acid esters.[96]

New possibilities for the qualitative and quantitative determination of covalent perchlorates appeared after the development of spectroscopic techniques. The IR spectra of individual alkyl perchlorates were first obtained by Radell et al.[67] and intense absorption bands at 1230 and 1260 cm,$^{-1}$ [$\nu_{as}(ClO_3)$], in the range 1000 to 1100 cm^{-1} [$\nu_s(ClO_3)$], and near 700 cm^{-1} [ν(Cl—O)], characteristic of covalent organic perchlorates, were found. There are no absorption bands in the range 1200—1300 cm^{-1} in the spectra of inorganic perchlorates. Subsequently, it was shown for a large number of perchlorates that intense bands in the range 1200—1300 cm^{-1} are present in the spectra of covalent organic perchlorates of any structure with different substituents[11,13,51] and can be used for the identification of these compounds.

Exceptional possibilities for the identification of perchloric acid esters are provided by NMR.[11,13,50,51,55,104] The presence of an electron-accepting substituent in the molecule (the perchloryloxy-group) results in a pronounced downfield shift of the signal. Thus the chemical shift of the α-proton attached to the perchloryloxy-group (solution in carbon tetrachloride) is 4.2 p.p.m. for methyl perchlorate and from 4.4 to 4.6 p.p.m. for n-alkyl perchlorates.[51] In the presence of a second electron-accepting substituent, the signal of the α-proton at the perchloryloxy-group shifts downfield even further; for example, it is 5.17 p.p.m. for 1-chloro-2-propyl perchlorate,[55] 5.56 p.p.m. for 2-fluoro-2,2-dinitroethyl perchlorate,[51] 6.3 p.p.m. for methylene diperchlorate, and 5.1—5.4 p.p.m. for arenesulphonylmethyl perchlorates.[11] ^{1}H NMR is very convenient for the determination of the yields of perchlorates without isolation from solution by integrating the spectrum of the specimen using a quantitative internal standard.[50,51,54,55,87,101–103]

Mass-spectrometric studies have been carried out only for perfluoroalkyl perchlorates[12,13,88,95] and β-bromoethyl perchlorate.[35] Molecular peaks have been detected in the mass spectra of trifluoromethyl perchlorate[12] and β-bromoethyl perchlorate.[35] Mass spectrometric data for the decomposition of perfluoroalkyl perchlorates with formation of the ClO_3^+, ClO_2^+, and ClO^+ fragments, but not ClO_4^+, have been used[12] to confirm their covalent structure.

Thin-layer[14,15,50,74] and gas—liquid[51,54] chromatographic methods have been employed for the identification and purification of covalent perchlorates. The thin-layer chromatography has proved very useful for the qualitative detection of covalent perchlorates: a characteristic property of these compounds is decomposition with formation of a black spot on moderate heating (100—150 °C) of the plate.[15,35]

Elemental analysis by combustion of the specimen has proved possible for the stable sulphonylmethyl,[11] perhalogenoalkyl,[12] and certain other perchlorates.[14,15,51,55,56]

X-Ray diffraction analysis has been used in recent years to establish the structures of a series of covalent perchlorates.[16,108,113–116] As a result of these investigations, the structures of toluene-*p*-sulphonylmethyl perchlorate[108] the skeletal perchlorate (XIII) of the trisecododecahedrane series,[16] as well as a series of skeletal secondary perchlorates having the tetracyclo[6.1.1.$0^{2,7}$0^{5,10}]-decane (XXXI) [113,114] and tetracyclo[5.3.0.$0^{2,5}$0^{3,8}]decane (XXXI) [115,116] carbon skeletons have been determined unambiguously.

3. Chemical Properties of Covalent Perchlorates

(a) General characteristics of the reactivity of covalent perchlorates. In the first studies on perchloric acid esters, it was already observed that these compounds are extremely reactive and enter especially readily into nucleophilic substitution reactions with water[23,96] and alcohols:[24]

$$Alk\,OClO_3 + ROH \rightarrow Alk\,OR + HClO_4,$$
$$R = H,\ Alk.$$

It was shown later that alkyl perchlorates exhibit a strong alkylating activity in relation to aromatic compounds.[65,111,112]

The high reactivity of covalent perchlorates, manifested even in reactions with weak nucleophiles, is due primarily to the fact that the perchlorate anion is a very effective leaving group or, in other words, is highly nucleofugitive. The alkylating capacity of covalent perchlorates varies within very broad limits as a function of the nature of the substituents and the structure of the carbon skeleton. t-Alkylperchlorates[51,62] as well as perchlorates of the allyl[71] and benzyl[106,107] series showed the most striking alkylating activity. The reactions of these perchlorates with nucleophiles apparently proceed via an S_N1 mechanism. Alkyl perchlorates with normal and secondary structures are less reactive and a bimolecular mechanism of the nucleophilic substitution of the perchlorate group is more characteristic of them. The introduction into the molecule of electron-accepting substituents such as a halogen[95,117] and the sulphonyl[10] or carboxy-groups[118] reduces the reactivity of the covalent perchlorate sharply: the abstraction of the ClO_4 group from the carbon atom in these perchlorates is very difficult and processes involving the dissociation of the $O-ClO_3$ bond become preferable.[10,117,118] Certain skeletal perchlorates [for example, compounds (XXXI) and (XXXII)], whose structural features hinder the attack by the nucleophile on the reaction centre, also exhibit a reduced reactivity.[118,119]

The reactions of covalent perchlorates have been studied in greatest detail in relation to methyl perchlorate[19-22,120-128] for a number of reasons. Firstly, methyl perchlorate is capable of undergoing nucleophilic substitution reactions even with very weakly nucleophilic species,[19,78,119,120,129,130] which permits the use of this compound as the substrate for kinetic studies designed to determine the nucleophilicity parameters in S_N2 processes.[121-124] Secondly, the markedly nucleofugitive properties of the perchlorate anion lead to certain anomalies in the kinetics of processes involving the nucleophilic substitution of the perchlorate group, which were initially actually interpreted as evidence in suport of a unimolecular reaction mechanism[123,124] and subsequently stimulated discussion[21,22,64,125] and a more profound study of these processes.[22] Finally, the perchlorate anion has solvation characteristics anomalous for an effective leaving group[126] and this leads to certain characteristic features of the kinetics of the hydrolysis of methyl perchlorate which are of theoretical interest.[19,126]

(b) Solvolysis of covalent perchlorates. Covalent perchlorates frequently enter into nucleophilic substitution reactions even with weakly nucleophilic species such as water and alcohol molecules. The highly nucleofugitive nature of the perchlorate anion leads to certain characteristics of the mechanisms of these processes. The problem of the solvolysis of covalent perchlorates attracted much attention after the publication of the studies[121-124] in 1967–1969 in which it was concluded, from a comparison of the activation entropies for the reactions of methyl perchlorate with certain nucleophiles, that the hydrolysis of this compound has an S_N1 mechanism in contrast to the S_N2 mechanism of methanolysis. This conclusion encountered sharp criticism[21,22,64,131] and gave rise to a number of kinetic studies devoted to a deeper understanding of the mechanism of the solvolysis of methyl perchlorate.[20-22,130,132] The rates of hydrolysis of methyl and ethyl perchlorates have been compared to determine the molecularity of the hydrolysis of methyl perchlorate.[64] In the case of a unimolecular mechanism, one would expect an appreciable acceleration of the hydrolysis after the introduction of the methyl group into the molecule, while for an S_N2 mechanism significant changes in rate in any direction can be usually observed. It was found[64] that the ratio of the rate constants for the hydrolysis of methyl and ethyl perchlorates is 0.8, which is within the limits established for a bimolecular mechanism in relation to a wide variety of leaving groups.

An alternative explanation of the kinetic features of the hydrolysis of methyl perchlorate in terms of Sneen's S_N2C^+ ion-pair mechanism.[133] However, this interpretation appears extremely unconvincing and has been justifiably rejected.[22,130,134] Kinetic data and especially data on the secondary isotope effect, which is observed in the hydrolysis of methyl perchlorate, have been explained within the framework of the traditional S_N2 mechanism and the hypothesis that the transition state in this reaction is looser than usual.[22] A more profound study of the nature of the transition state in the solvolysis of methyl perchlorate has been carried out using isotope effect data.[127] The values of the m constant in the Grunwald–Winstein equation, characterising the nature of the substrate, were used as evidence for the traditional S_N2 mechanism of the hydrolysis.[20,130] For the hydrolysis of methyl perchlorates in the methanol–water system, $m = 0.11$, which is characteristic of a typical S_N2 reaction. On the other hand, in the case of the S_N1 or the S_N2C^+ ion-pair mechanism one would expect $m = 1$.[130] In careful investigation of the kinetics of the solvolysis of covalent perchlorates in solvent systems with different ionising powers Y, a maximum was observed on the plots of the solvolysis rate constant against Y.[20,130] The presence of a region in which the rate of hydrolysis diminishses with increase in the concentration of water in the aprotic solvent (acetone or dioxan) was explained[20,130] by the unusual solvation characteristics of the perchlorate ion, which is more effectively solvated in a dipolar aprotic solvent than in water.[134]

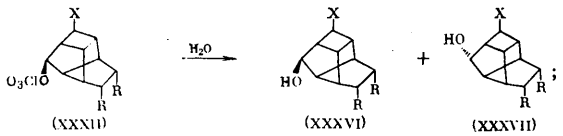
The substitution of a hydrogen atom in methyl perchlorate by an electron-accepting group, such as the sulphonyl[10] and trifluoromethyl[171] groups, leads to other pathways in the solvolytic processes. In such cases, the oxidation-reduction decomposition with elimination of the chlorate anion becomes preferable.

The mechanism of the solvolysis of arenesulphonylmethyl perchlorates has been studied in greatest detail.[11,135-141] The rate of solvolysis of these compounds is determined by the slow stage involving the deprotonation of the methylene group; the carbanion formed decomposes rapidly with formation of the chlorate anion, formic acid (or alkyl formate if the reaction is carried out in alcohol), and arenesulphonic acid.[135-141]

$$ArSO_2CH_2OClO_3 + ROH \rightarrow ArSO_2\bar{C}HOClO_3 + R\overset{+}{O}H_2$$
$$\downarrow ROH$$
$$ArSO_2H + HCOOR + ClO_3^-;$$
$$Ar = p\text{-}NO_2C_6H_4, p\text{-}CH_3C_6H_4;\ R = H, CH_3, C_2H_5, t\text{-}C_4H_9, n\text{-}C_5H_{11}, CF_3CH_2.$$

This pathway is apparently associated with the increased acidity of the methylene protons in arenesulphonylmethyl perchlorates as a consequence of the presence of two strong electron-accepting substituents in the molecule.

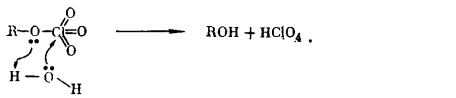
The pathway followed in the solvolysis of secondary perchlorates has been investigated solely in relation to skeletal perchlorates of the type (XXXI) and (XXXII), obtained by reactions involving the coupled electrophilic addition of the perchlorate group to olefins by the authors of the present review.[118] We investigated the reactions of covalent skeletal secondary perchlorates with water and $H_2{}^{18}O$ in acetone and dimethyl sulphoxide (DMSO) under various conditions. In all cases, the stereoisomeric hydroxy-derivatives (XXXVI) and (XXXVII) were isolated as the reaction products, the reaction in acetone proceeding preferentially with retention of configuration of the reaction centre and in DMSO with its inversion:



(XXXII) (XXXVI) (XXXVII)

X=Ar,I; R=CH_3,CO_2CH_3.

The absence of selectivity in the hydrolysis and the results obtained for the distribution of the ^{18}O label can be explained[118] with the aid of a mechanism involving the attack by a water molecule on the chlorine atom in the perchlorate group:



Examples of such reactions in the series of inorganic perchloric acid derivatives are known,[51,53,54] but for covalent organic perchlorates the occurrence of processes determined by the attack on the chlorine atom by the nucleophile were not observed previously.

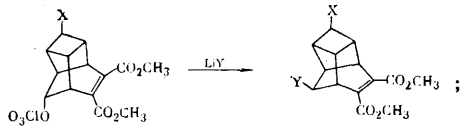
(c) Nucleophilic substitution reactions. Processes involving nucleophilic substitution in covalent perchlorates are of both theoretical[19,78,120,121,123,124] and practical[4,76,77] interest due to the high reactivity of these compounds. The kinetics of the reactions of methyl perchlorate with more than 20 different nucleophiles have been studied[123,124] in water and methanol in order to test the applicability of the Swain–Scott equation.[25] It was noted[123,124] that the rates of reaction of methyl perchlorate depend relatively slightly on the nature of the nucleophile, which is consistent with the idea that the perchlorate anion is a very effective leaving group. On the whole, it is concluded that these reactions have an S_N2 mechanism and that it is impossible to construct a general series in terms of the strength of the nucleophiles from the processes investigated.

The study of the kinetics of the reactions of methyl perchlorate with amines in water and methanol led to the conclusion[121] that these reactions, carried out with 25 amines, have a bimolecular mechanism. However, in the case of ammonia and butylamine the author put forward the hypothesis that there may be competition between S_N2 and S_N1 mechanisms. This hypothesis is doubtful bearing in mind the results of the polemics on the hydrolysis of methyl perchlorate (see the previous Section).

The kinetics of the reactions of a series of alkyl perchlorates (methyl, ethyl, isopropyl, and 2-adamantyl perchlorates) with *NN*-dimethylaniline in benzene have been studied recently.[19] On the basis of the kinetic parameters and especially the absence of an appreciable H/D isotope effect, it was shown that these reactions proceed via a classical S_N2 mechanism and that the second order rate constants decrease in the sequence Me > Et > iso-Pr $\gg$ 2-Ad.

The high reactivity of the covalent perchlorates is clearly manifested in relation to their reactions with weak nucleophiles such as arenesulphonate anions.[119,120] In a study of the kinetics of the reactions of various tetrabutylammonium arenesulphonates with methyl perchlorate in acetonitrile, the reaction was found to be of second order and it was established that the rate constants are independent of the concentration of the salt.[120] On the other hand, in the bimolecular reaction of silver toluene-*p*-sulphonate with methyl perchlorate, a decrease in the rate constant was observed with increase in the concentration of silver toluene-*p*-sulphonate, which is apparently a consequence of the decrease in the nucleophilicity of the anion as a result of the formation of close ion pairs with the silver cation.

The present authors investigated the stereochemistry of the reactions of skeletal covalent secondary perchlorates with a series of nucleophiles, including arenesulphonate anions (in relation to the toluene-*p*-sulphonate anion.[119] It was shown that the reactions of the perchlorates (XXXI) and (XXXII) with the nucleophiles proceed with complete inversion of the configuration at the reaction centre, which constitutes convincing evidence in support of the S_N2 mechanism:



(XXXI), X=SAr; Y=Cl,Br.



(XXXII). X=SAr,I; R=CH_3,CO_2CH_3; Y=Cl,Br, p-NO_2-$C_6H_4SO_3^-$.

The reactions investigated can serve as a convenient method for introducing various substituents into the molecule of a skeletal compound.

Several studies in which covalent compounds were used for synthetic purposes as alkylating agents have been published in recent years.[76,77] For example, methyl perchlorate can be used to alkylate sugars[77] and certain heterocyclic compounds.[76] Unfortunately, the number of such studies is very limited, but further investigations in this field will undoubtedly lead to the discovery of new synthetic applications of the highly reactive covalent organic perchlorates.

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It is seen from the data examined in this review that covalent organic perchlorates have become a class of accessible compounds suitable for various chemical reactions. Although the possibilities for their practical application are held back by the potential and frequently real risk of explosion of perchloric acid esters, nevertheless in most cases this obstacle can be readily eliminated by employing them without intermediate isolation in the form of safe solutions in inert solvents. Furthermore, studies on the reactivity of covalent perchlorates have demonstrated that the perchlorate anion is one of the best leaving groups. The data obtained constitute a basis for the practical utilisation of covalent perchlorates in synthesis as reagents with a stronger alkylating activity than the traditional toluene-*p*-sulphonates and other organic sulphonates. Another distinctive feature is that substitution in perchloric acid esters takes place via an S_N mechanism. Thus a basis has been created for stereospecific syntheses, which also constitutes an advantage of alkyl perchlorates over traditional alkylating agents.

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Aryl Derivatives of Thallium(III): Preparation and Use in Organic Synthesis

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The review presents new data on the preparation of aryl derivatives of thallium(III) and their application in organic synthesis, which is based on the possibility of the selective introduction of an organic group into an aromatic ring by replacing the thallium atom in arylthallium compounds. Processes involving the modification of aromatic compounds in the presence of thallium salts are also considered. The probable mechanisms of the reactions occurring in such processes are discussed. The bibliography includes 97 references.

CONTENTS

I. Synthesis of compounds of the type $ArTlX_2$ 1054
II. Synthesis of compounds of the type Ar_2TlX 1059
III. Synthesis of triarylthallium compounds Ar_3Tl 1060
IV. Applications of arylthallium(III) compounds in organic synthesis 1061

I. SYNTHESIS OF COMPOUNDS OF THE TYPE $ArTlX_2$

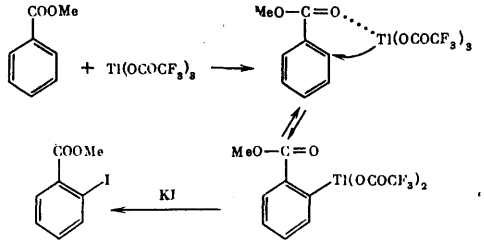
1. Reactions Involving Direction Thallation of Arenes

The commonest method of synthesis of compounds of the type $ArTlX_2$ and one which has been investigated in greatest detail is the direct thallation of arenes by trivalent thallium salts. The most convenient system for this purpose comprises thallium trifluoroacetate (TTFA) in trifluoroacetic acid (TFAA).[1-4]

In contrast to arenes activated by electron-donating substituents, which are thallated at room temperature in several minutes, the complete conversion of halogenobenzenes was attained in 48 h at room temperature or in 30 min in boiling TFAA. Substrates with a nucleus deactivated with respect to electrophilic substitution, such as benzoic acid and ααα-trifluorotoluene react with TTFA in boiling TFAA in 21 and 98 h respectively.

The reaction involving the substitution of the thallium atom by an iodine atom can be used to establish the position of substitution in the aromatic ring on thallation. The authors suggest the following methods of synthesis of aryl iodides from the arylthallium bis(trifluoroacetates) obtained depending on the properties of the latter: (a) treatment of the reaction mixture with an aqueous KI solution after the completion of thallation without isolating the products—for arylthallium bis(trifluoroacetates) soluble in CF_3COOH; (b) isolation, drying, and interaction with KI in an aqueous acetone solution—for products crystallising from the reaction mixture; (c) the addition of KI to the reaction mixture in acetonitrile—for aromatic systems sensitive to the action of acids.

The effect of the substituent in the aromatic nucleus on the isomeric composition of the thallation products has been investigated.[3] In the thallation of benzoic acid by treatment with TTFA in TFAA, it was established that substitution takes place mainly in the *ortho*-position in the aromatic ring. It was postulated initially that a mixed thallium(III) carboxylate is formed during the reaction and then donates the thallium atom to the *ortho*-position. However, the thallation of methyl benzoate also affords mainly the *ortho*-products. Bearing this finding in mind, the following reaction mechanism has been suggested:[3]



The isomeric composition of the products formed on thallation of aromatic compounds is presented in Table 1.

Analysis of the data in Table 1 for the thallation-iodination† of the homologous series of phenyl-containing carboxylic acids (compounds 4, 5, 10, and 11 in Table 1) shows that the degree of *ortho*-substitution depends appreciably on the chain length of the carboxyl-containing group, since the carboxy-group is a complex-forming agent in relation to TTFA. In fact, an intermediate is formed in the σ-complex formation stage in which the Tl atom is linked to a carbon atom of the arene and is coordinated to the carbonyl O atom in the side chain of the substitutuent. Such intermediate complexes have been called[3] "chelate intermediates". Thus, whereas benzoic and phenylacetic acids and the corresponding methyl esters afford exclusively *ortho*-derivatives via five- or six-membered "chelate" rings, the *ortho*-thallation of phenylpropionic acid can proceed only via the formation of a seven-membered "chelate" ring, which is less preferable and this in fact entails a decrease in the content of the *ortho*-thallation product (29%).

† By the term thallation-iodination, the authors denote the preliminary thallation of the substrate followed by the treatment of the compounds obtained with KI using one of the methods described by McKillop et al.[2]

The behaviour of a whole series of aromatic compounds containing substituents in the side chain, which are capable of forming complexes with TTFA, has been investigated[3] from the standpoint of the possible supply of the thallium atom to the ring via a "chelate intermediate" formed by the Lewis acid (TTFA) and an oxygen-containing Lewis base. Thus substrates capable of forming five- and six-membered intermediate chelates give rise almost exclusively to *ortho*-substitution products (compounds 15, 17, 22, and 23 in Table 1). The increase in the chain length of the intermediate chelate leads to a sharp fall of the yield of the *ortho*-isomer (compounds 10, 11, 18, and 20 in Table 1). The degree of *ortho*-substitution depends also on the nature of the Lewis base in the side chain of the substrate and decreases in the sequence ester, acid, ether, alcohol. Intramolecular thallation via a "chelate ring" is extremely sensitive to steric factors. Thus the replacement of one α-hydrogen atom in phenylacetic acid by the methyl group results in a decrease in the degree of *ortho*-substitution from 92 to 65%, while the replacement of the second α-hydrogen atom by the methyl group altogether inhibits *ortho*-substitution.

Table 1. The isomeric composition of the products of the thallation of the arenes C_6H_5R at room temperature.[3]

No.	R	Proportions of isomers, %		
		ortho	*meta*	*para*
1	CH_3	9	4	87
2	$CH_2CH_2CH_3$	3	6	91
3	$CH(CH_3)_2$	1	5	94
4	COOH	95	5	0
5	CH_2COOH	92	3	5
6	$CH(CH_3)COOH$	65	11	24
7	$C(CH_3)_2COOH$	0	37	63
8	CH_2CH_2COOH	29	13	58
9	$CH(CH_3)CH_2COOH$	37	14	49
10	$CH_2CH_2CH_2COOH$	6	10	84
11	$CH_2CH_2CH_2CH_2COOH$	5	9	86
12	$COOCH_3$	95	5	0
13	CH_2COOCH_3	92	3	5
14	$CH_2CH_2COOCH_3$	53	7	40
15	CH_2OH	99	—	—
16	CH_2OCOCH_3	50	21	29
17	CH_2CH_2OH	83	6	11
18	$CH_2CH_2OCOCH_3$	3	13	84
19	$CH_2CH_2CH_2OH$	10	10	80
20	$CH_2CH_2CH_2OCOCH_3$	5	12	83
21	OCH_3	7	0	93
22	CH_2OCH_3	99	—	—
23	$CH_2CH_2OCH_3$	85	3	12
24	$CH_2CH_2CH_2OCH_3$	27	6	67
25	CH_2OCOCF_3	49	24	27
26	$OCOCH_3$	21	0	79
27	—*	31% thallation in the 6-position		

*2-$CH_3C_6H_4CH_2COOH$.

The intermediate formation of a "chelate" ring is supported by the following results: firstly, the thallation of compounds containing in the side chain activated substituents incapable of forming "chelate complexes" with TTFA takes place in several minutes at room temperature, while the presence of a Lewis base in the side chain appreciably increases the thallation time regardless of the size of the ring which may be formed. Secondly, the degree of *meta*-substitution is highest when there is a possibility of the formation of an eight-membered "chelate" (compounds 8, 16, 18, and 25 in Table 1) and also in those cases where *ortho*-thallation via a "chelate complex" is hindered by steric factors (compounds 6 and 7 in Table 1). The thallation of cumene (compound 3 in Table 1), which has a bulky substitutuent incapable of forming a complex with thallium-(III), affords only 5% of the *meta*-isomer. The authors conclude that thallation is a process much more sensitive to steric factors than mercuration.

Thallation under the conditions of kinetic control leads to the initial preferential formation of *ortho*- and *para*-isomers. Since thallation is reversible, an increase in temperature to 73 °C (boiling CF_3COOH) increases the fraction of the *meta*-isomer, i.e. in this case thermodynamic control plays a significant role.

It is noteworthy that thallation of a substrate containing in the side chain substituents capable of complex formation requires additional time for the attainment of equilibrium. This finding imposes definite synthetic limitations on the *meta*-thallation process, since TTFA decomposes after prolonged heating in TFAA. Thallation of β-phenylethyl acetate (compound 18 in Table 1) under the conditions of kinetic control leads to substitution in the *para*-position of the aromatic ring (84%), which is associated with the increase in ring size in the *ortho*-thallation intermediate from six-membered for β-phenyl-ethanol (compound 17 in Table 1) to eight-membered in its acetate.

Thus variation of the thallation conditions (thermodynamic and kinetic control) makes it possible to introduce a thallium atom selectively in a specific position in the aromatic nucleus.

Thallium(III) acetate in acetic acid containing added $HClO_4$ has been used[5] as a thallating agent. In this case, thallation also proceeds smoothly, especially in the case of arenes activated with respect to electrophilic substitution. The products isolated were characterised as the monohydrates of mixed arylthallium acetate perchlorates. The highest yield of the arylthallium compounds is attained at room temperature. An increase in temperature entails a decrease in yield owing to the occurrence of side processes such as the coupling of aromatic radicals and the oxidation of the solvent with formation of a thallium(I) salt.

A series of kinetic studies of the influence of various additives on the course of thallation have been carried out. The thallation of arenes in various acids has been investigated.[6] Heating of thallium-(III) acetate with benzene in 1 M H_2SO_4 leads to the rapid precipitation of a deposit containing $PhTl(HSO_4)_2$, Ph_2TlHSO_4, and $Tl(HSO_4)_3$. Heating of benzene with a thallium(III) salt in perchloric acid affords a mixture of phenylthallium dichloride with diphenylthallium chloride.

It has been established[6] that the rate of thallation increases with increase in temperature to a greater extent for an activated aromatic compound (toluene) than for a non-activated one (benzoic acid). This fact can be associated both with the electronic effects of the substituents and with the possible formation of an intermediate chelate complex.[3] An approximate estimate of the rates of thallation and mercuration in aqueous $HClO_4$ demonstrated that the rate of mercuration under identical conditions is approximately 200–400 times higher than the rate of thallation.

The influence of catalytic strong acid additives on the rate of thallation has been investigated.[7,8] The authors showed that perchloric acid is a more active thallation catalyst than sulphuric acid. The mechanism of the catalysis consists in the formation of polar electrophilic species which are involved in an acid–base

equilibrium:

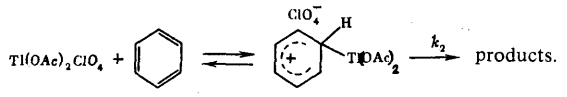
$$\begin{array}{l} Tl(OAc)_3 \rightleftarrows [Tl^{-}(OAc)_2^{-}OAc] \rightleftarrows Tl^{+}(OAc)_2 + OAc^{-}, \\ K_4\downarrow\uparrow \\ Tl(OAc)_2ClO_4 \rightleftarrows [Tl^{+}(OAc)_2ClO_4^{-}] \rightleftarrows Tl^{+}(OAc)_2 + ClO_4^{-}, \\ K_5\downarrow\uparrow \\ Tl(OAc)(ClO_4)_2 \rightleftarrows [Tl^{2+}(OAc)\,2ClO_4^{-}] \rightleftarrows Tl^{2+}(OAc) + 2ClO_4^{-}, \\ K_6\downarrow\uparrow \\ Tl(ClO_4)_3 \rightleftarrows [Tl^{3-}3ClO_4^{-}] \rightleftarrows Tl^{3+} + 3ClO_4^{-}. \end{array}$$

The values of K_1 were calculated for the *p*-nitroaniline–perchloric acid–thallium(III) acetate system. On the assumption that $Tl(OAc)_2ClO_4$ does not react with the indicator, K_1 = 4.6–5.0 litre mol^{-1}; on the other hand, if $Tl(OAc)_2ClO_4$ does react with the indicator, like $Tl(OAc)_3$, then the constants K_1 are between 6.0 and 8.4 litre mol^{-1}.

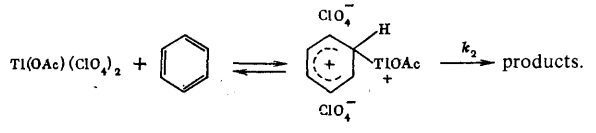
The data obtained show that the constants K_1 and K_2 are important for the determination of the character of the equilibrium in solution and hence of the thallation process itself, since at high catalyst concentrations the content of the $Tl(OAc)_2X$ species increases – the degree of conversion of $Tl(OAc)_3$ into $Tl(OAc)_2X$ is 92% for [HX] = 0.5 M. The data for the conductivities of the solutions permit the conclusion that in pure acetic acid, thallation is effected by the electrophile in the form of an ion pair, while in dilute solutions ionic species are active.

It follows from the activation parameters E_a and $\Delta S^{\neq}$ that more than one electrophilic species is involved in the thallation process. At low catalyst concentrations the process is characterised by high values of E_a and an appreciable positive entropy, while at high concentrations, where the catalyst is most effective, the values of E_a are comparatively low but $\Delta S^{\neq}$ also diminishes appreciably. According to the authors, the rate-limiting stage of the process is the decomposition of Wheland's intermediate, characterised by the constant k_2 (Schemes 1 and 2). The authors describe the process by Scheme 1 at low catalyst concentrations and by Scheme 2 at high concentrations:

Scheme 1



Scheme 2



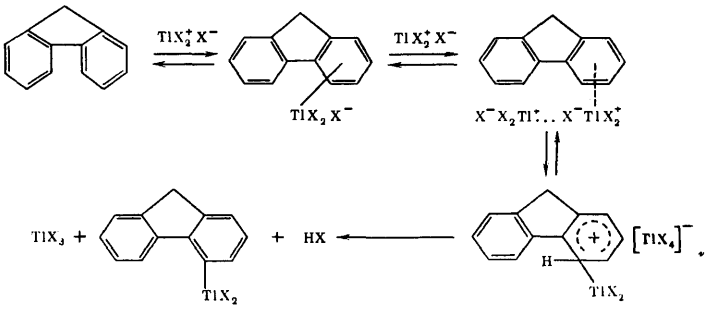
In their study of the variation of the isomeric composition of the toluene thallation products with time, the authors found that *para*-thallation initially predominates, its extent falling with time and with decrease in the catalyst concentration. Thus thallation for 24 h at an H_2SO_4 concentration of 2 M leads to the following proportions of the isomers: 18.7% *ortho*, 6.4% *meta*, and 75% *para*; when $[H_2SO_4]$ = 0.4 M, the proportions are 37.6, 3.4, and 59% respectively.

The kinetics of the thallation of fluorene by thallium(III) acetate in aqueous acetic acid have been investigated.[9] The authors observed that the reaction is of first order with respect to the substrate and of second with respect to thallium triacetate; its rate is described by the equation

$$v = k_3[Tl(III)]^2[\text{fluorene}].$$

The addition of strong protic acids sharply accelerates thallation; the reaction is of sixth order with respect to sulphuric acid. The reaction mechanism described by Scheme 3 was put forward:

Scheme 3



The second order with respect to the thallating agent agrees with the assumption of the participation of two and more electrophilic species in the thallation process,[8] but the influence of the second electrophile molecule may also be different than that suggested by Narasumnau et al.[9] In principle, there is a possibility of the formation of a dimeric species (Scheme 4) which is a stronger electrophile than the initial thallium(III) salt:

Scheme 4

$$2TlX_3 \rightleftarrows Tl_2X_6 \quad \text{or} \quad [TlX_2]^{+}[TlX_4]^{-}.$$

In a study of the thallation of activated arenes by TTFA in TFAA, the formation of the aromatic radical-cation Ar^{+} in the reaction mixture was detected by EPR.[10] According to the authors, the reaction proceeds via a one-electron transfer stage:

Scheme 5

$$Tl^{III} + ArH \rightleftarrows [ArH\cdot Tl^{III}];\ [ArH\cdot Tl^{III}] \rightleftarrows [ArH^{+\cdot}Tl^{II}],$$

$$[ArH^{+\cdot}Tl^{II}] \begin{cases} \longrightarrow Tl^{II} + ArH^{+} \\ \longrightarrow Ar^{+}{}_{Tl^{III}}{}^{H} \xrightarrow[-H^{+}]{} ArTl^{III} \end{cases}$$

The authors suggest that the electron transfer stage is an obligatory process both for aromatic thallation and for the formation of Ar^{+}.

This concept was developed further in a study[11] where the interaction of the homologous series of methylbenzenes $C_6H_n(Me)_{6-n}$ with TTFA was investigated. It was shown that the active electrophilic species in this process is the cation $[Tl(OCOCF_3)_2]^{+}$, formed as a result of the reversible reaction

$$TTFA \rightleftarrows [Tl(OCOCF_3)_2]^{+} + CF_3COO^{-}\ (K).$$

The constant K at 25 °C in TFAA is 1×10^{-3} mol $litre^{-1}$. According to the authors,[11] further reactions are associated with the formation of a π-complex between the arene and $[Tl(OCOCF_3)_2]^{+}$, which decomposes in accordance with Scheme 5. Kinetic data characterising the electrophilic thallation and electron transfer pathways have been published.[11]

The relative rates of thallation of toluene and benzene (k_t/k_b) as well as the partial rates of formation of the isomers in the thallation of toluene with TTFA in TFAA have been determined.[12] The ratios k_t/k_b determined by Kwok et al.[12] and Olah et al.[13] are 43.5 and 33 respectively; the partial rate factors for the thallation of toluene at 25 °C were found to be 12.7, 4.5, and 226 by Kwok et al.[12] and 9.6, 5.7, and 168 by Olah et al.[13] for *ortho*-, *meta*-, and *para*-substitution respectively; this enabled Kwok et al.[12] to conclude that the aromatic thallation reaction proceeds via an aromatic electrophilic substitution mechanism, most probably via a Wheland intermediate, in contrast to the mechanism proposed by Kochi and coworkers.[10,11]

Roberts[14] investigated the kinetics of the thallation of arenes by NMR. He suggests that the data obtained by this method can describe the thallation process more accurately, since in this instance there is no need to treat the reaction mixture with KI and to determine the kinetic parameters of the reaction with respect to the iodoarene formed. It was found that $k_t/k_b = 24$. Roberts[14] explains the increase in k_t/k_b with increase in acid concentration, observed by Briody and Moore,[8] by the influence of the large positive charge on the thallium atom, i.e. in the first stage of the interaction of the electrophile and the substrate, the electrostatic interaction forces should play an appreciable role according to the author.

The kinetic isotope effect, obtained by Roberts, is 5.0 (3.7 according to Briody and Moore[8]). The authors suggest that the rate-limiting stage of the thallation process is proton transfer in a transition complex analogous to a Wheland intermediate.

The time variation of the isomeric composition of the products has also been investigated for toluene. Thus the *ortho*:*meta*:*para* ratios are 28:29:63 after 13 min and 31:38:31 after 5000 min.

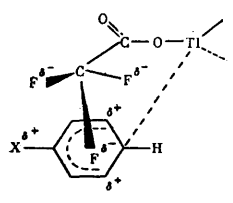
The kinetics of the thallation of a wide range of substrates by treatment with TTFA using both NMR and other methods for the detection of products were investigated in detail in a later study.[15] $Tl(OAc)_3.1.5H_2O$ was chosen as the thallating agent, since, according to the authors, it is more stable than TTFA. Furthermore, it was shown[15] that the rates of thallation of arenes by thallium(III) acetate sesquihydrate in TFAA agree with the rates of thallation of the same arenes by treatment with TTFA in TFAA.

The process mechanism was represented as follows:[15]

$$ArH + TlX_3 \overset{K_1}{\rightleftarrows} \pi\text{-complex} \overset{k_2}{\rightarrow} \text{products}.$$

The values of K_1 and k_2 found in the above study are listed in Table 2.

On the basis of the Hammett and Yukawa-Tsuno parameters, the authors concluded that there is an appreciable charge separation in each phase of the reaction, especially in the π-complex formation stage:



(A)

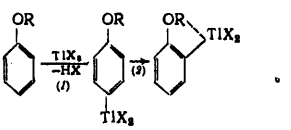
Analysis of the activation parameters for the reaction showed that, whereas the activation energies for mercuration and thallation are approximately equal, the activation entropy is much higher in absolute magnitude for thallation (−11.9 cal mol^{-1} K^{-1}) than for mercuration (−1.2 cal mol^{-1} K^{-1}). The appreciable, compared with mercuration, charge transfer in the intermediate (A) is responsible for this effect. Ultimately the stability of the complex (A) is higher than the stability of the analogous complex in the mercuration reaction and this contributes to the entropy factor.

Table 2. The values of K_1 and k_2 for the thallation of the arenes C_6H_5R.[15]

No.	R	10^2k_2, s^{-1}	K_1, litre mol^{-1}
1	H	1.04	1.9
2	Me	0.166	2.7
3	Et	10.1	10.7
4	t-Bu	12.3	12.9
5	F	0.176	1.18
6	Cl	0.0733	0.70
7	Br	0.0469	0.89

The thallation of a series of aromatic substrates by TTFA in TFAA, leading to a disubstituted product, has been investigated.[16] Dithalation takes place in the presence of an excess of $Tl(OCOCF_3)_3$; 2,4-bis[(trifluoroacetato)thallio]anisole and 2,4-bis-[(trifluoroacetato)thallio]phenetole were isolated in the case of anisole and phenetole in 70 and 50% yields respectively. The complete dithalation of thiophen has been achieved in acetonitrile; the occurrence of dithallation has been demonstrated by the formation of diiodothiophen. Partial dithallation of benzene, toluene, and *m*-xylene has been observed when they were treated with an excess of TTFA in boiling TFAA.

In the thallation of anisole with an equivalent amount of TTFA, Deacon et al.[16] observed that an appreciable amount of the *para*-substitution product is formed in the first stage of the reaction and that only then is there an increase in the content of the *o*-thallated anisole, which is apparently more stable by virtue of the intramolecular oxygen–thallium coordination with formation of a four-membered chelate ring:



The authors support their view that the thermodynamic stability of *o*-anisylthallium bis(trifluoroacetate) is higher than that of its *p*-isomer by the results of a study[17] in which the interaction of phenylthallium bis(trifluoroacetate) with anisole, leading to the formation of *o*-anisylthallium bis(trifluoroacetate), was described. It is suggested[16] that reaction (2) proceeds via a mechanism different from that of the rearrangement of the *p*-thallated product to the *m*-isomer or of the preferential *ortho*-thallation of substituted arenes via five- and six-membered chelate rings.[3]

It has been suggested that thallium(III) trichloroacetate in trichloroacetic acid be used to thallate benzene and toluene.[18] The reaction takes place smoothly at room temperature, the yields of the

products are about 70%, and the ratios of the isomers for toluene are *ortho : meta : para* = 9 : 5 : 86. However, the synthetic use of the thallium(III) trichloroacetate/trichloroacetic acid system is limited by the electronic influence of the substituents in the aromatic ring. Thus anisole, nitrobenzene, and methyl benzoate do not enter into the thallation reaction under the given conditions.

It has been noted[6,10,11] that the aromatic radicals are coupled to form biaryls in the interaction of arenes, activated by electron-donating substituents, with TTFA and that for many arenes of this kind the above reaction predominates over the electrophilic thallation process (see below). A method has been proposed[19] for the thallation of activated arenes. The suppression of oxidative dimerisation is achieved by using TTFA in an ether/TFAA mixture. The coloured ethereal solution of TTFA and the substrate is usually treated with TFAA before the formation of a colourless solution and the precipitation of a deposit (the thallated arene) or the substrate is added to TTFA in a 2/1 ether/TFAA mixture.

Whereas a whole series of thallating agents in different media can be used for the thallation of arenes activated by electron-donating substituents, the direct thallation of polyfluoroarenes is extremely difficult owing to the inactivity of the aromatic ring with respect to electrophilic substitution. Direct thallation of polyfluoroarenes has been achieved by using a new thalating agent—thallium(III) triflate:[20,21]

$$RH + Tl(O_3SCF_3)_3 \xrightarrow{CF_3COOH} RTl(O_3SCF_3)_2 + CF_3SO_3H,$$
$$R = p\text{-}MeOC_6F_4, p\text{-}MeC_6F_4, m\text{-}HC_6F_4, p\text{-}HC_6F_4, C_6F_5, 3,5\text{-}H_2C_6F_3, 3,6\text{-}H_2C_6F_3.$$

The authors established a qualitative reactivity series for the arenes investigated in the thallation reaction:

$$C_6H_6 > p\text{-}MeOC_6F_4H > 1,2,4\text{-}F_3C_6H_3 \cong 1,3,5\text{-}F_3C_6H_3 > m\text{-}H_2C_6F_4;$$
$$p\text{-}MeC_6F_4H > o\text{-}H_2C_6F_4 > C_6F_5H \geqslant p\text{-}H_2C_6H_4 > m\text{-}O_2NC_6F_4H.$$

They were unable to isolate polyfluorophenylthallium bis(trifluoromethanesulphonates) in a pure form because, after the removal of the solvent, the product remained contaminated by trifluoroacetate impurities and the attempt at crystallisation led to the symmetrisation of the product to bis(pentafluorophenyl)thallium salts. The direct thallation products are therefore characterised by NMR, conversion into the corresponding aryl iodides by treatment with KI, and symmetrisation to bis(pentafluorophenyl)thallium salts.

The highest yield of thallation products was attained in boiling TFAA, but under these conditions *m*-BrC_6F_4H and *m*-$O_2NC_6F_4H$ do not react. The use of trifluoromethanesulphonic acid as the solvent leads to the oxidation of the substrates by the thallium(III) salts to the corresponding phenols. Although, after the conversion of the thallation products by treatment with $Tl(O_3SCF_3)_3$ to aryl iodides the yields of the latter are high, presumably the degree of thallation of polyfluoroarenes is in fact higher still, since a reaction of polyfluorophenylthallium salts with I^-, in which iodine-containing products are not formed, is known.[22]

2. Substitution of the Anion in Arylthallium Bis(trifluoroacetates)

One of the known methods of synthesis of compounds of the type $ArTlX_2$ involves the substitution of the anion in arylthallium bis(trifluoroacetates). The stability of compounds of the type $ArTlX_2$ as a function of the nature of X has been investigated.[23] When X = I, arylthallium compounds are extremely unstable, which had been noted earlier (see, for example, McKillop et al.[2]), so that their decomposition is a preparative method of synthesis of aryl iodides and constitutes a test reaction for the thallation of the aromatic ring. However, one should note the relative stability of $C_6F_5TlI_2$. A stable compound containing the ArTlI fragment has been synthesised.[24] The Ar—Tl—I bond system is stabilised by introducing into the coordination sphere a complex-forming molecule—dibenzo-18-crown-6 ether (DBC):

$$PhTlO + HClO_4 + DBC \xrightarrow{H_2O} [PhTl(DBC)OH]ClO_4 \cdot H_2O \xrightarrow[MeCN]{Na(15\text{-crown-}5)I} [PhTl(DBC)I]ClO_4.$$

The properties of stabilised complexes of the type $[p\text{-}RC_6H_4Tl(L)X]^+$, where R = H or Me, X = Cl, Br, I, SPh, or OH, and L = dibenzo-18-crown-6 ether, have been investigated.[25] For R = H and X = I, the photolysis or pyrolysis of the initial complex leads mainly to iodobenzene, while in the case where X = Br and especially Cl only insignificant amounts of the corresponding halogenobenzenes are produced:

$$[PhTl(L)I]^+ \rightleftarrows [PhTl(L)]^+ \rightarrow PhTl^+$$
$$\downarrow \qquad\qquad \downarrow I^-$$
$$Ph^- \xrightarrow{I^-} PhI$$

The reduction of the complex in which R = Me and X = OH by treatment with $P(OMe)_3$, ascorbic acid, and *N*-benzyl-1,4-dihydronicotinamide affords toluene as the main product, while the analogous reduction of the cation $ArTlX^+$, unstabilised by L, leads to Ar_2TlX.

Arylthallium dibromides are also extremely unstable and readily decompose, affording aryl bromides and small amounts of diarylthallium bromides (15—20%), while arylthallium dichlorides are extremely stable.[23]

A convenient preparative method has been developed for the synthesis of arylthallium dihalides:[26]

$$ArTlCl_2 \xleftarrow{Me_3SiCl} ArTl(OCOMe)_2 \xrightarrow{R_4SnBr_2} ArTlBr_2.$$

The yields of the dihalides obtained by this method are quantitative; the target products, precipitated during the reaction, do not require additional purification.

A method has been proposed[27] for the synthesis of arylthallium diacetates from asymmetric organotin compounds:

$$Ar_2SnR_2 + Tl(OCOMe)_3 \rightarrow ArTl(OCOMe)_2.$$

The alkyl substituent is not split off from the tin atom, the more nucleophilic aryl group being transferred to the thallium atom.

By varying the reactant ratio, it is possible to obtain by this method the acylates of both mono- and di-phenylthallium. The target products crystallise from the reaction mixture and do not require additional purification, but the use of this method is limited by the availability of the organotin compound.

Compounds of the type $ArTlX_2$, where X is a halogen or an organic acid residue, can also be obtained from organomercury, organotin, and organoboron compounds. These methods of synthesis are generally accepted and have been described in detail in a monograph.[28]

II. SYNTHESIS OF COMPOUNDS OF THE TYPE AR_2TlX

1. Synthesis with the Aid of Organometallic Compounds

Compounds of the type Ar_2TlX are the most widely distributed class of organothallium compounds. There exists a whole series of methods of synthesis of these thallium(III) derivatives from organolithium, -magnesium, -zinc, -mercury, -boron, -aluminium, and -tin compounds, the procedures involved in the use of which have been described in detail in a monograph.[28] Methods in which organolithium, -magnesium, -boron, and -mercury compounds are used are the most convenient among them for the preparation of diarylthallium salts:

$$2ArM + TlX_3 \rightarrow Ar_2TlX + 2MX,$$
$$M = Li, MgX, B(OR)_2, HgAr.$$

In recent years, diarylthallium compounds have been synthesised via other organometallic derivatives not so much for the preparation of previously unknown diarlythallium salts as with the aim of creating model compounds for physicochemical studies, e.g. X-ray diffraction. Thus the X-ray diffraction analysis of the complexes of bis(pentafluorophenyl)thallium chlorides and bromides with triphenylphosphine oxide has been carried out.[29,30] Bis(pentafluorophenyl)thallium chlorides and bromides were obtained from thallium(III) salts and the pentafluorophenyl Grignard reagent. The complexes investigated are dimeric compounds with asymmetric chlorine bridges; the thallium atom in these compounds has a coordination number of 5.

The synthesis of diarylthallium trifluoroacetates from TTFA and arylmagnesium halide leads to the target products in satisfactory yields (50–70%), but it takes place in several stages owing to the difficulty of exchanging the Br^- anion for trifluoroacetate:[31]

$$ArMgBr \xrightarrow[Et_2O]{Tl(OCOCF_3)_3} Ar_2TlBr \xrightarrow[EtOH-H_2O]{KOH} Ar_2TlOH \xrightarrow{CF_3COOH} \rightarrow Ar_2Tl(OCOCF_3).$$

The symmetrisation of monoarylthallium derivatives is a more convenient method of synthesis of diarylthallium trifluoroacetates.

2. Symmetrisation of Monoarylthallium Salts

The spontaneous disproportionation of compounds of the type $ArTlX_2$ to Ar_2TlX is widely known,[28] but it had not been used previously as a preparative method. In many cases symmetrisation is a more convenient method than organometallic synthesis. Thus, in order to obtain diarylthallium trifluoroacetates via a Grignard reagent, a three-stage synthesis is required,[31] while refluxing of arylthallium bis(trifluoroacetate) in acetone for 30 min affords diarylthallium trifluoroacetates in 50–90% yields:[31]

$$2ArTlX_2 \rightarrow Ar_2TlX + TlX_3,$$
$$Ar = 4\text{-}MeC_6H_4, 3.4\text{-}Me_2C_6H_3, 2.4\text{-}Me_2C_6H_3, 2,5\text{-}Me_2C_6H_3; X = CF_3COO$$

It has been suggested that trimethyl phosphite, under the influence of which diarylthallium trifluoroacetate is formed from ArTl.$(OCOCF_3)_2$ in several minutes at room temperature in a nearly quantitative yield, be used as the symmetrising agent.[23]

An attempt was made later[32] to investigate the mechanism of the disproportionation of monoarylthallium compounds. It had been suggested earlier[23] that the role of trimethyl phosphite consists in reducing TlX_3 to a thallium(I) compound, which displaces an equilibrium of the type:

$$2ArTlX_2 \rightleftarrows Ar_2TlX + TlX_3.$$

According to the authors,[32] this reaction mechanism is unlikely, because they failed to observe spectroscopic evidence for the spontaneous disproportionation of the starting material. They therefore assumed that the complex $RTlX_2.P(OR)_3$ is formed in the first stage, as a result of which the electron density on the Tl atom increases and the reduction of thalium(III) to thallium(I) is promoted. It is suggested that in this complex the carbon–thallium bond becomes more accessible to electophilic attack by a proton or another thallium atom. However, it is not clear at which stage of the reaction such attack takes place—before reduction, synchronously with reduction, or after it. According to the authors, the electrophilic attack by a proton before the reduction of thallium(III) is unlikely, since the initial complex $RTlX_2.L$ should interact more readily with the electrophile than the product $R_2TlX.L$, and yet it is stable under the protolysis conditions.

The interaction of $RTl(OAc)_2$ with nucleophiles capable of coordination can also lead to the symmetrisation of the starting material instead of the expected nucleophilic substitution of thallium:[32]

$$RTl(OAc)_2 + NaSPh \rightarrow R_2TlX.$$

The authors were unable to determine the nature of X, but they suggest that it is a thiophenoxide.

It is noteworthy that phosphorous acid esters are not universal symmetrising agents for arylthallium compounds. Polyfluorophenylthallium bis(trifluoromethanesulphonates) are not symmetrised on refluxing in acetone and on treatment with $P(OR)_3$ but such symmetrisation can be readily achieved by treatment with sodium acetate in boiling water, affording bis(polyfluorophenyl)thallium acetate.[21] $(3,5\text{-}H_2C_6F_3)Tl(O_3SCF_3)_2$, which does not undergo symmetrisation but exchanges the anion and the metal atom, affording as a result the corresponding diacetate, is an exception.

3. Reactions Associated with the Exchange of an Anion at the Thallium Atom

The substitution of an anion at a thallium atom is an extremely convenient preparative method of synthesis of various diarylthallium salts. Of the relatively recent studies, mention should be made of the synthesis of various derivatives of bis(polychlorophenyl)-thallium:[33]

$$(C_6Cl_5)_2TlCl + AgX \rightarrow (C_6Cl_5)_2TlX + AgCl;$$
$$X = MeCOO, ClO_4, 1/2SO_4.$$

Bis(pentachlorophenyl)thallium perchlorate proved to be a convenient starting compound for the substitution of an anion, which cannot be achieved by treating $(C_6Cl_5)_2TlCl$ with silver salts:

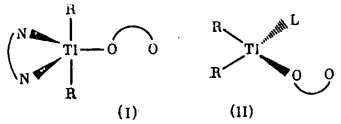
$$(C_6Cl_5)_2TlClO_4 + KX \rightarrow (C_6Cl_5)_2TlX + KClO_4;$$
$$X = I, Br, CN.$$

The substitution of an acetate residue by a halogen can be readily carried out by treating diarylthallium acylates with Me_3SiCl or R_2SnBr_2.[26] A new method of synthesis of such acylates has been proposed.[27]

Bis(pentafluorophenyl)thallium compounds $(C_6F_5)_2TlX$ (X = $CF_3COCHCOMe$, $CF_3COCHCOCF_3$, or PhCOCHCOMe) have been obtained by the reaction of $(C_6F_5)_2TlBr$ with the salts of diketones. They form stable complexes with αα-bipyridyl (bipy) and *o*-phenanthroline (phen).[34] The thallium salts of sulphinic acids, obtained as a result of ion exchange, also form stable complexes with bipy and phen:[35]

$$Ar_2TlBr + AgO_2SR \rightarrow Ar_2TlO_2SR + AgBr,$$
$$Ar = C_6H_5, C_6F_5;\ R = C_6H_5,\ 4\text{-}MeC_6H_4.$$
$$Ar_2TlO_2SR + L \rightarrow Ar_2Tl(L)O_2SR,$$
$$L = bipy,\ Ph_3PO,\ Ph_3AsO,\ phen.$$

The structure (I) with a 5-coordinated thallium atom for the complex with a bidentate ligand and the structure (II) for the complex with a monodentate ligand have been proposed from IR and NMR data:[35]



(I) (II)

The authors[35] also synthesised thallium(I) salts of sulphinic acids, but spectroscopic data do not provide a clear idea about their structure.

On heating, the thallium salts of sulphinic acid readily evolve SO_2, which has been used to synthesise bis(polyfluorophenyl)thallium acetates:[36]

$$2C_6F_nH_{5-n}SO_2Li + 3Tl(OCOCF_3)_3 \xrightarrow{MeCO_2H} (C_6F_nH_{5-n})_2TlO_2CMe +$$
$$+ CF_3COOH + 2SO_2 + 2LiOCOCF_3.$$

It has been found[35] that the highest yields of the target product are attained when the ratio of the initial reactants is Li : Tl = 2 : 3.

Later the reaction developed in the above study[36] was used to synthesise various dimesitylthallium salts.

Bis(polyfluorophenyl)thallium polyfluorobenzoates have been obtained by substituting an anion at the metal atom:[38]

$$R_2TlX + NaO_2CR \rightarrow R_2TlO_2CR + NaX;$$
$$R = C_6F_5, p\text{-}MeOC_6F_4, p\text{-}HC_6F_4, o\text{-}HC_6F_4, m\text{-}HC_6F_4.$$

4. The Synthesis of "Mixed" Diarylthallium Compounds Ar(Ar')TlX

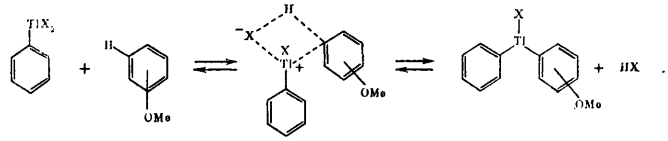
"Mixed" diarylthallium compounds Ar(Ar')TlX have been obtained by the reaction of monoarylthallium salts with aryl-boronic acids:[39,40]

$$ArTlX_2 + Ar'B(OH)_2 \rightarrow Ar(Ar')TlX.$$

They are less stable than Ar_2TlX and disproportionate after a time:

$$2Ar(Ar')TlX \rightarrow Ar_2TlX + Ar'_2TlX.$$

The thallation of anisole by phenylthallium bis(trifluoroacetate), leading to the formation of a mixed product—phenyl(anisyl)-thallium trifluoroacetate—has been investigated.[41] The formation of the target product was inferred from the amount of phenyl and anisyl iodides after treating the reaction mixture with the I_2/KI system. The authors propose the following process mechanism:



The use of chlorobenzene as the substrate does not lead to a "mixed" phenyl(chlorophenyl)thallium product and only the exchange of the aryl groups at the metal atom is observed:

$$PhCl + PhTlX_2 \rightleftarrows ClC_6H_4TlX_2 + PhH.$$

An analogous exchange of the aryl groups at the thallium atom had been noted earlier.[17]

"Mixed" aryl(*B*-carbaboranyl)thallium salts have been synthesised in accordance with the scheme[42]

$$RC{-}CR + PhMgBr \rightarrow RC{-}CR$$
$$B_{10}H_9Tl(OCOCF_3)_2 \qquad B_{10}H_9Tl(Br)Ph$$

III. SYNTHESIS OF TRIARYLTHALLIUM COMPOUNDS Ar_3Tl

Virtually no new methods of synthesis of compounds of the type Ar_3Tl have been proposed during the last 15 years. This is because the traditional methods of synthesis of such compounds,[28] especially via the organolithium, organosodium, and organomagnesium compounds, are sufficiently convenient and the use of triarylthallium derivatives in synthesis is insignificant. Nevertheless, several recent studies were devoted to the synthesis of compounds of the type Ar_3Tl.

Tris(polyfluorophenyl)thallium compounds have been obtained by the reaction of bis(polyfluorophenyl)thallium salts with metallic compounds:[43]

$$2R_2TlBr + 2Cu + C_4H_8O_2 \rightarrow 2R_3Tl \cdot C_4H_8O_2 + TlBr + 2CuBr.$$

The replacement of the complex-forming solvent (ether, dioxan) by toluene alters significantly the course of the reaction:

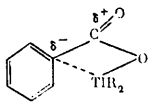
$$(C_6F_5)_2TlBr \xrightarrow[PhMe]{Cu} (C_6F_5)_2 + TlBr.$$

The attempts to symmetrise R_2TlBr, where R = *o*-HC_6F_4 or 2,5-$H_2C_6F_3$, were unsuccessful. The authors suggest that R_3Tl is formed via an intermediate organocopper compound. This hypothesis is supported by the formation of $(C_6F_5)_2$ in toluene, since it is known that bis(pentafluorophenyl)thallium bromide does not by itself decompose on refluxing in toluene.[44] In view of the dependence of the symmetrisation on the degree of substitution of the aromatic ring by fluorine atoms, the authors suggest the involvement of carbanionic species in the transition state. In their view, the reaction mechanism involves the coordination of thallium to copper atoms, the subsequent transfer of the polyfluorophenyl group to

copper, and electron transfer from thallium to copper:

$$R_2TlBr + Cu \rightarrow 2RCu + TlBr,$$
$$R_2TlBr + RCu \rightarrow R_3Tl + CuBr.$$

A convenient method of synthesis of tri(polyfluorophenyl)thallium involves the refluxing of bis(polyfluorophenyl)thallium benzoate in pyridine.[38] The rate of decarboxylation diminishes in the following sequence of groups R: $C_6F_5 \simeq p\text{-}MeOC_6F_4 > p\text{-}HC_6F_4 > m\text{-}HC_6F_4 \gg o\text{-}HC_6F_4$, i.e. with decrease in the -I effect of the group. This finding shows that the aryl residue in the transition state is carbanionic:



(III)

Another possible process mechanism involves the participation of the free carbanion, which captures the R_2Tl^+ species faster than it can decompose:

Scheme 6

$$R_2TlO_2CR \rightleftarrows R_2Tl^+ + RCO_2^-;\ RCO_2^- \rightarrow R^- + CO_2;$$
$$R^- + R_2Tl^+ \rightarrow R_3Tl;\ R^- + R_2TlO_2CR \rightarrow R_3Tl + RCO_2^-.$$

The rapid decarboxylation of pentafluorophenylbenzoic acid in pyridine, which apparently proceeds via pyridinium pentafluorophenylbenzoate, supports Scheme 6 according to the authors, although the formation of ion pairs may lead to a transition complex of type (III). Pyrolysis of R_2TlO_2Cr without a solvent leads to a significant yield of R_3Tl only for R = C_6S_5 (40%), while in the remaining cases the reaction products are polyarylenes.

The stability of tris(polychlorophenyl)thallium in air was unexpected.[45] The synthesis of stable compounds containing four pentafluorophenyl groups at the thallium atom has been described:[46]

$$Tl(C_6F_5)_2Br + 2C_6F_5Li \xrightarrow{QX} Q[Tl(C_6F_5)_4],$$
$$X = Cl, Br;\ Q = Et_4N,\ Ph_3PCH_2Ph.$$

The preparation of complexes of the type $R_3Tl(diox)$, where R = C_6F_5 or 2,4,6-$F_3C_6H_2$, has been described.[47] For R = C_6F_5, the reaction of RLi with $TlCl_3$ leads to a mixture of the products $Bu_4N[TlR_4]$ and $(Bu_4N)_3[TlR_6]$, while in the case where R = 2,4,6-$F_3C_6H_2$, the product is exclusively R_3Tl. The complexes $R_3Tl(diox)$ have been obtained either by adding dioxan to R_3Tl in ether (R = 2,4,6-$F_3C_6H_2$) or in accordance with the scheme

$$Bu_4NTl(C_6F_5)_4 + HBF_4 \xrightarrow{dioxan} Tl(C_6F_5)_3(diox) + Bu_4NBF_4 + C_6F_5H.$$

The reactions involving the substitution of the dioxan ligand lead to:

(a) neutral thallium(III) complexes:

$$R_3Tl(diox) + L \rightarrow R_3Tl(L) + diox;$$
$$L = Ph_3PO,\ Py,\ PPh_3,\ (Ph_2P)_2CH_2;$$

(b) anionic complexes:

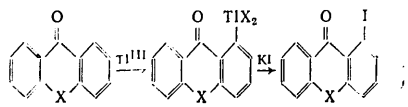
$$R_3Tl(diox) + QX \rightarrow Q[TlR_3(X)] + dioxan;$$
$$Q = Bu_4N,\ (PPh_3)_2N;\ X = Cl, CN;$$
$$Q[TlR_3(CN)] + AgX \xrightarrow{-AgCN} \begin{cases} \xrightarrow{X=Cl} QX + TlR_3 \\ \xrightarrow{X=CF_3COO} Q[TlR_3(X)] \end{cases},$$

(c) anionic complexes with a thallium–transition metal bond:

$$R_3Tl(diox) + QM^* \rightarrow Q[R_3Tl{-}M^*] + dioxan$$
$$R = 2,4,6\text{-}F_3C_6H_2,\ M^* = [MoCp(CO)_3]^-,\ [WCp(CO)_3]^-,\ [Mn(CO)_5]^-;$$
$$R = C_6F_5,\ M^* = [MoCp(CO)_3]^-,\ [WCp(CO)_3]^-.$$
$$Tl(C_6F_5)_3 + QM^* \rightarrow Q[(C_6F_5)_3Tl{-}M^*],$$
$$M^* = [Co(CO)_4]^-.$$

IV. APPLICATIONS OF ARYLTHALLIUM(III) COMPOUNDS IN ORGANIC SYNTHESIS

The possibility of substituting the thallium atom in arylthallium derivatives by an organic group has opened a pathway to the selective introduction of a substituent into the aromatic ring, since thallation itself is a selective process. McKillop, Taylor, and coworkers[1] have shown that, when arylthallium bis(trifluoroacetates) are treated with KI, the iodine atom replaces thallium in the aromatic ring. The thallation-iodination reaction has been used successfully for the selective introduction of iodine into the aromatic ring of diaryl ketones:[48]



X=CMe_2, $(CH_2)_2$, S.

The intermediate arylthallium compound formed when an organic substituent is introduced into the aromatic ring is not always isolated. Thus, in the synthesis of phenols,[49] the authors began with the corresponding arenes and TTFA:

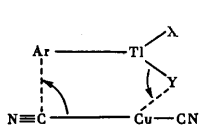
$$PhH \xrightarrow[CF_3COOH]{Tl(OCOCF_3)_3} PhTl(OCOCF_3)_2 \xrightarrow[PPh_3]{Pb(OAc)_4} PhOCOCF_3 \xrightarrow{NaOH} PhOH.$$

The yields of the phenols were 50–80%.

The attempt to obtain aromatic nitriles by the pyrolysis of $[ArTl.(CN)_3]K$ or $ArTl(CN)_2$ ws unsuccessful but the photolysis of a 1% aqueous solution of arylthallium bis(trifluoroacetate) in the presence of 25 equivalents of KCN led to the formation of aromatic nitriles in 50–80% yields. Traces of benzene, cyanobiphenyl, and phenol were detected as side products in the reaction mixture.[49] In order to obtain cyanoarenes, the reaction of $ArTl(OAc)ClO_4H_2O$ with bivalent or monovalent copper cyanides was also used[50] (Scheme 7, see below):

$$ArTlX_2 \xrightarrow[MeCN(pyridine)]{CuCN(Cu(CN)_2)} ArCN.$$

The highest yields of aryl cyanides are obtained when pyridine is used as the solvent. A free radical pathway to the formation of aryl cyanides is thought[50] to be unlikely since neither biphenyl nor benzene were detected in the reaction mixture. Nor were the transfer of the aryl group to acrylonitrile and the polymerisation of acrylonitrile observed. According to the authors, the interaction of the substrate with $Cu(CN)_2$ proceeds via the cyclic transition state

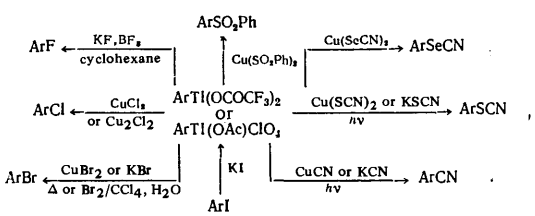


In contrast to the method of Uemura et al.,[50] which is limited by the relatively weak thallating capacity of $Tl(OAc)_2ClO_4$, Taylor et al.[51] obtained the nitriles over a wide range of arenes, both electron-deficient and electron-saturated. An increase in the types of aromatic substrates has been achieved[51] by using a more universal thallating agent—TTFA. The essential feature of the method consists in the refluxing of the thallated substrate with CuCN in acetonitrile for 2–17 h. The proposed reaction mechanism is

$$PhTlX_2 \xrightarrow[-[Cu^{II}CN]^+]{CuCN} [PhTlX \xrightarrow[-TlX]{} Ph^{\cdot}] \xrightarrow[-Cu^+]{^{\cdot}CuCN} PhCN.$$

The intermediate formation of an aryl complex of thallium(II) is postulated; the homolysis of the C–Tl bond in the complex leads to the formation of Ar·—an intermediate in the Rosenmund–von Braun reaction. In those cases where thallation in acetonitrile is impossible, the reaction was carried out in two stages: (1) thallation by treatment with TTFA in TFAA and isolation of the thallated products; (2) reaction with CuCN in acetonitrile; if the thallation is carried out in acetonitrile, the isolation stage is not required and the interaction with CuCN takes place *in situ*. The yields of the nitriles are 60–90% (Scheme 7):

Scheme 7



Aryl thiocyanates have been obtained by the photolysis of a solution of arylthallium bis(trifluoroacetates) in the presence of potassium thiocyanate[52] and on refluxing $ArTl(OAc)ClO_4$ with $Cu(SCN)_2$ in dioxan:[53]

$$\left.\begin{array}{l} ArTl(OCOCF_3)_2 \xrightarrow{h\nu, KSCN} \\ ArTl(OAc)ClO_4 \xrightarrow{Cu(SCN)_2} \end{array}\right\} \rightarrow ArSCN.$$

The yields of aryl thiocyantes are 50–80%.

Phenyl and tolyl selenocyanates have been obtained from phenyl- and tolyl-thallium bis(trifluoroacetates) by treatment with Cu(SeCN) in dioxan.[18]

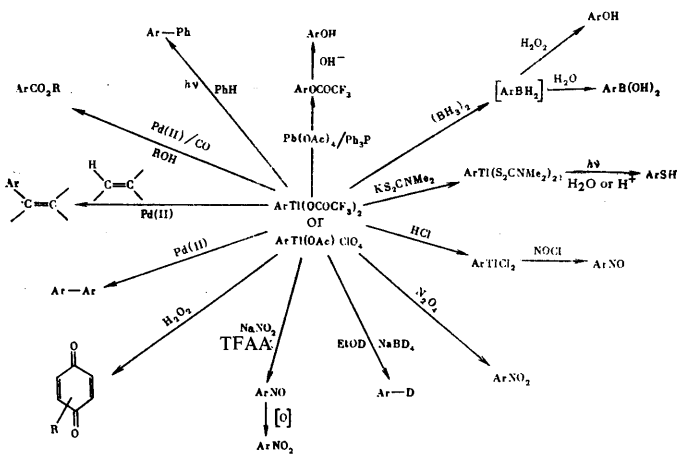
Arylthallium bis(trifluoroacetates) proved to be convenient initial compounds for the preparation of nitrosoarenes:[54]

$$ArTl(OCOCF_3)_2 \xrightarrow{HCl} ArTlCl_2 \xrightarrow[CHCl_3]{NOCl} ArNO.$$

Since the thallium derivatives of substituted arenes can be isolated comparatively readily in an isomerically pure form, this method is very much more selective than the direct nitrosation of arenes.

Nitroarenes have been obtained for the reaction of arylthallium bis(trifluoroacetates) with NO_2 [55] (yields 50–90%) (Scheme 8, see below). It has been shown in relation to tolylthallium bis(trifluoroacetates) that the main reaction product is *p*-nitrotoluene, but the refluxing of a solution of the thallated substrates before nitration entails some increase in the fraction of the *meta*-isomer. Treatment of the reaction mixture with NO_2 without isolating arylthallium bis(trifluoroacetate) also led to a satisfactory yield of the corresponding nitroarenes in which the *para*-product preominated. Direct nitration of arenes does not involve a selectivity as high as that which can be achieved using arylthallium compounds. Treatment of the products of the thallation of ethylbenzene with NO_2 affords nitroethylbenzenes with the isomers in the proportions $o:m:p$ = 5.3:1.7:93 for an overall yield of 76%, while the direct nitration of ethylbenzene by treatment with NO_2 in CF_3COOH leads to the isomer ratios $o:m:p$ = 42.5:2.0:55.5 for an overall yield of 11%.[55]

Scheme 8



Aromatic nitro-compounds have been obtained by the reaction of an arylthallium substrate with $NaNO_3$, KNO_2, or $AgNO_2$ in trifluoroacetic acid[56,57] (Scheme 8):

$$ArTl(OAc)ClO_4 \xrightarrow[CF_3COOH]{NaNO_2} ArNO_2.$$

It has been established for Ar-*p*-$CH_3C_6H_4$ that the nitro-group replaces the thallium atom and traces of *o*- and *m*-nitrotoluenes were not observed. In contrast to the halogenodethallation[58] and pseudohalogenodethallation[50,53] reactions (Scheme 7), the replacement of thallium by the nitro-group does not occur in organic solvents such as pyridine, dioxan, and dimethylformamide (DMF) even on refluxing. In the case of anisylthallium derivatives, the corresponding nitroarenes were obtained, but the formation of significant amounts of nitroso-derivatives was also noted. The addition of potassium dichromate to the reaction mixture makes it possible to obtain only the nitro-derivatives of anisole. The authors suggest that the action of potassium dichromate does not reduce to simple oxidation of the nitroso-group to the nitro-group; $K_2Cr_2O_7$ probably oxidises the C–Tl bond and then follows attack by NO_2^- in accordance with the scheme proposed for arylpalladium derivatives.[59]

The reaction of arylthallium diacetate with $Me_2CNO_2^-$ on irradiation by the light of a xenon lamp with ordinary glass leads to the formation of 2-arylnitropropanes:[60]

$$ArTl(OAc)_2 + Me_2CNO_2^- \rightarrow ArCMe_2NO_2.$$

The formation of the radical $C_6HMe_4NO^{\cdot}$ has been detected by EPR in the presence of nitrosodurene, which indicates a radical process mechanism:

$$ArTl(OAc)_2 + R_2CNO_2^- \rightarrow ArTlOAc + OAc^- + R_2CNO_2^{\cdot},$$
$$ArTlOAc \rightarrow Ar^{\cdot} + TlOAc,$$
$$Ar^{\cdot} + R_2CNO_2^{\cdot} \rightarrow ArCMe_2NO_2.$$

The product yields are 60–70%. In the absence of irradiation, up to 20% of arylthallium diacetate is formed.

The radical cleavage of the C–Tl bond on UV irradiation is a characteristic feature of arylthallium compounds. Thus irradiation of a suspension of arylthallium bis(trifluoroacetates) in aqueous ammonia results in the formation of aromatic amines.[61] A method of synthesis of aniline and phenol has been proposed.[62] Its essential feature consists in the reaction of the thallated arene in an aqueous or organic medium with a nucleophile (NH_3, H_2O), which results in the formation of the products of the nucleophilic substitution of thallium. The reaction was carried out at relatively low temperatures (200 °C) in steel reactors in the presence of promoting additives such as CuCl, $FeCl_2.4H_2O$, etc. When the reaction is carried out in an aqueous medium, the main products are phenols, while in methane or benzene, in the presence of a suitable promoting agent, for example, $CuCl_2$, the main product proved to be aniline.

The photolysis of arylthallium bis(*NN*-dimethyldithiocarbamates)[61] leads to thiophenols, while arylthallium difluorides are stable under the photolysis and pyrolysis conditions.[63] Fluoroarenes have been synthesised (in 40–90% yield) by refluxing arylthallium difluorides with dry BF_3 in cyclohexane (Scheme 7):[63]

$$ArTlF_2 \xrightarrow{BF_3} ArF.$$

The reaction of arylthallium substrates with palladium salts has come to be widely used in organic synthesis recently.

The interaction of monoarylthallium salts with palladium(II) chloride leads to the formation of biaryls in 40–60% yields:

$$ArTlX_2 \xrightarrow[NaOAc,AcOH]{PdCl_2} Ar{-}Ar + Pd^0 + Tl^I.$$

Apart from biaryls, ArH and ArX were detected as side products.

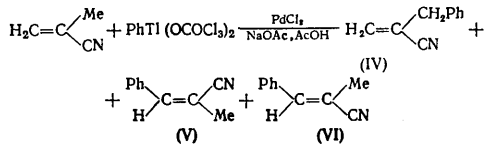
The authors showed that the nature of X does not have a significant influence on the yield of biaryls except in the case where X = Cl and Ar = Ph, where the yield of chlorobenzene is 30%.

The aryl group is transferred from arylthallium salts of olefins:[65]

$$ArTlX_2 + RCH{=}CHR' \xrightarrow[CuCl]{Li_2PdCl_4} ArCR{=}CHR';$$
Ar = Ph, *n*-MeC_6H_4, 1,3,5-$Me_3C_6H_2$; R = H, Ph;
R′ = CO_2Me, H; X = O_2CCF_3, O_2CMe, Cl, CN.

The authors showed that palladium(II) can be used in both catalytic and equimolecular amounts in relation to $ArTlX_2$. The olefins obtained have the *trans*-configuration.

The reaction of phenylthallium bis(trichloroacetates) with $PdCl_2$ in acetic acid in the presence of styrene affords exclusively *trans*-stilbene, while the analogous reaction with methacrylonitrile is not so selective:[18]



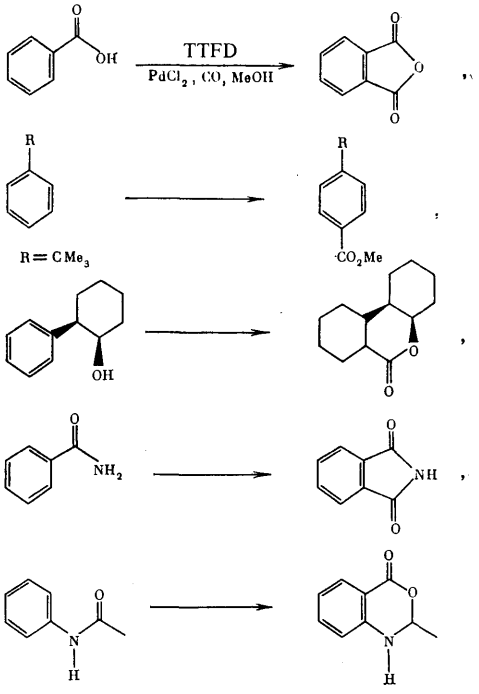
The ratios (IV):(V):(VI) = 55:26:19 are obtained. Analogous products have been prepared using metallic palladium as the catalyst.

The high selectivity of aromatic thallation and the ease of the exchange of thallium for palladium lead to extensive synthetic prospects for the use of the thallium(III)–palladium(II) system. A method has been proposed[66] for the synthesis of arenecarboxylic acids, consisting in the interaction of the arene with thallium(III) trifluoroacetate in the presence of catalytic amounts of palladium acetate under a CO pressure of 4–7 atm, but the selectivity of the method is low. The use of the analogous reaction under a CO pressure of 1 atm[67,68] made it possible to obtain a series of esters, lactones, and heterocyclic compounds, the reactions exhibiting high regio- and stereo-selectivities in many cases. In contrast to the study of Spencer and Thorpe,[65] the authors do not introduce an oxidant into the reaction mixture assuming that the zero-valent palladium formed is oxidised by the thallium(III) salt generated during the transmetallation of arylthallium bis(trifluoroacetate):

$$ArTlX_2 + PdX_4^{-2} \rightarrow ArPdX_3^{-2} + TlX_3,$$
$$ArPdX_3^{-2} + CO \rightarrow ArC(O)PdX_3^{-2},$$
$$ArC(O)PdX_3^{-2} + ROH \rightarrow ArC(O)OR + HX + Pd^0 + 2X^-,$$
$$Pd^0 + TlX_3 \rightarrow PdX_2 + TlX.$$

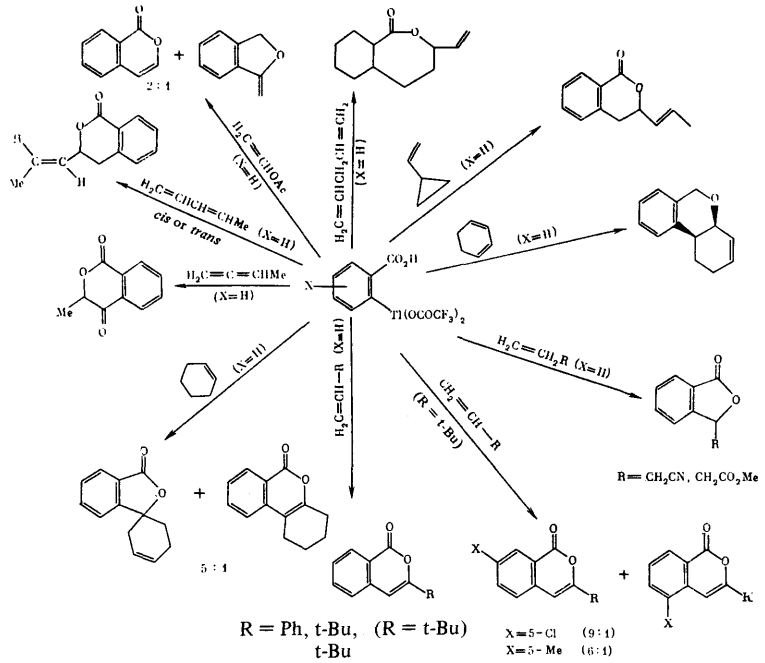
Biphenyl is a side product in this reaction, its formation being suppressed by the addition of LiCl and MgO. It has been found that the use of 0.1 of an equivalent of $PdCl_2$, 2 equivalents of LiCl, and one equivalent of MgO ensures product yields in excess of 90% (Scheme 9).

Scheme 9



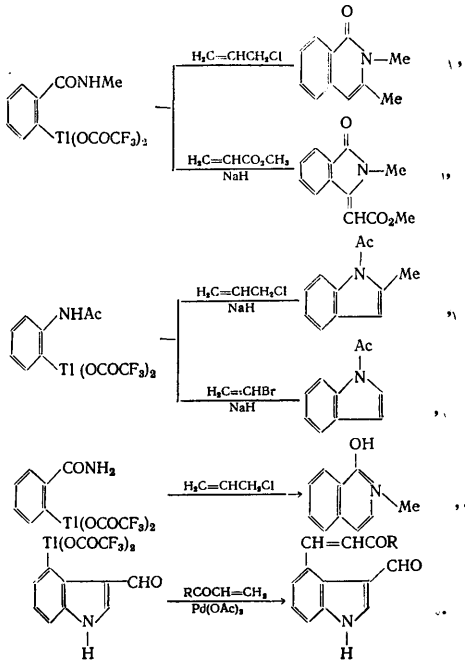
A method has also been developed for the synthesis of isocoumarins and 3,4-dihydrocoumarins from thallated benzoic acid, palladium(II) salts, and substituted olefins or cyclopropanes[69] (Scheme 10):

Scheme 10



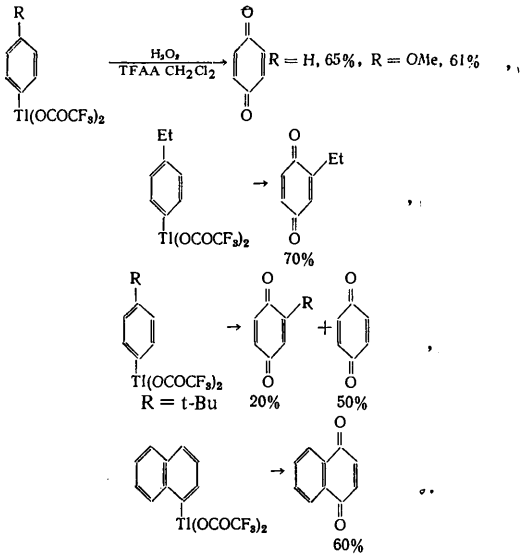
The reactions were usually carried out in acetonitrile with the ratio substrate: Li_2PdCl_4 = 1:1. In the successful synthetic procedure, the addition of 2 equivalents of Et_3N and Na_2CO_3 to the reaction mixture after the start of the reaction between the thallated substrate and the olefin makes it possible to cyclise the *o*-vinylbenzoic acids formed as side products to isocoumarin (Scheme 10). using an analogous method, isoquinolines and indoles have been obtained[70] (Scheme 11); the synthesis of substituted indoles containing a carbonyl group linked to the heterocyclic fragment has been described.[71]

Scheme 11



The oxidation of thallated arenes by H_2O_2 [72] is a fairly convenient method of synthesis of *p*-benzoquinones and in the course of the oxidation the alkyl substituent is either eliminated or migrates (Scheme 12).

Scheme 12



The presence of TTFA is known to ensure the selective bromination of aromatic compounds, while the oxidation of phenols by TTFA makes it possible to obtain a wide range of quinones. However, it has been shown that arylthallium derivatives were not formed in the course of these processes. The data on the bromination of arenes and the oxidation of phenols with particiption of TTFA have been surveyed.[4,73]

Ryabov et al.[74] were able to synthesise 4,4′-substituted biaryls by adding catalytic amounts of palladium(II) in the interaction of substituted arenes with TTFA:

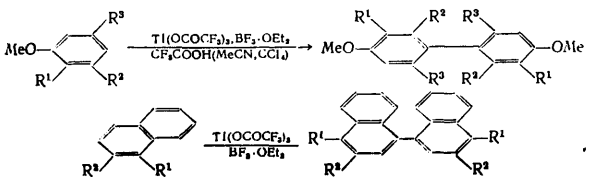
$$PhX + Tl(OCOCF_3)_3 \xrightarrow{10\%Pd(OAc)_2} XC_6H_4C_6H_4X,$$
$$X = Me, MeO, Cl, F, H.$$

The reaction takes place under mild conditions and the initial arene is used as the solvent. The proportions of the isomers in the arene coupling reaction under the influence of the TTFA/$Pd(OAc)_2$ system were investigated later[75,76] and the partial rate factors f_o, f_m, and f_p were determined in relation to the formation of bitolyl. The yield of 4,4′-bitolyl in the coupling of toluene on treatment with the Tl(III)/Pd(II) system is higher than in the presence of palladium(II) acetate or thallium(III) trifluoroacetate alone. It has been shown[76] that rapid thallation of the aromatic substrate takes place in the first stage, this being followed by the rate-limiting stage—the interaction of $ArTl(OCOCF_3)_2$ with the monomeric palladium diacetate [the $Pd_3(OAc)_6$ depolymerisation product]. The subsequent reactions of the arylpalladium intermediate lead to the observed reaction products. The thallation and transmetallation stages are characterised by rate constants which are respectively $-5.6(\sigma^+)$ and $-3.0(\sigma)$:

$$ArH + TlX_3 \rightarrow ArTlX_2 + HX,$$
$$Pd_3(OAc)_6 \rightleftarrows 3Pd(OAc)_2,$$
$$ArTlX_2 + Pd(OAc)_2 \xrightarrow{slow} ArPd(OAc) + TlX_2(OAc),$$
$$2ArPd(OAc) \xrightarrow{fast} Ar-Ar + Pd^0 + Pd(OAc)_2,$$
$$Pd^0 + Tl^{III} \xrightarrow{fast} Pd^{II} + Tl^{I}.$$

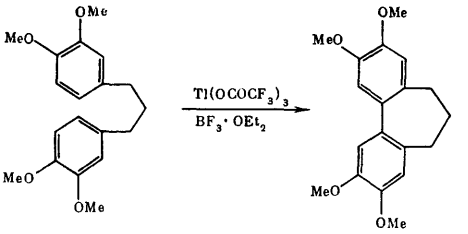
A whole series of studies have been devoted to the coupling of arenes to biaryls on treatment with arylthallium or thallium(III) salts. Thus the photolysis of arylthallium bis(trifluoroacetate) in benzene leads to asymmetric biaryls in 50–98% yields.[77] The reaction of an aromatic Grignard reagent with thallium monobromide in the tetrahydrofuran (THF)–benzene mixture affords biaryls in 70–90% yields.[78] The best reaction condition involves the addition of ArMgBr to a suspension of TlBr in the boiling solvent with the ratio ArMgBr : TlBr = 1 : 1.15. The reaction is complicated when an *o*-substituted organomagnesium compound is used; in this case, dehalogenation or the formation of diarylthallium bromide are observed. The cross-coupling of aryl groups can be achieved by this method. Thus the interaction of a mixture of phenyl- and *p*-anisyl-magnesium bromides with TlBr leads to a mixture of all the possible biaryls: 4-$MeOC_6H_4Ph$ (46%), PhPh (36%), and $(4\text{-}MeOC_6H_4)_2$ (18%).

It has been noted[6] that, when toluene is refluxed with thallium(III) acetate, a small amount of coupling products—isomeric bitolyls—is formed together with the main product—*p*-tolylthallium diacetate. The reaction of arenes containing strong electron-donating substituents with TTFA in TFAA, CCl_4, or acetonitrile with added boron trifluoride etherate leads to arene coupling products in 80–100% yields:[79]



The authors showed that the presence of electron-accepting substituents in the aromatic ring (COOR, CN, NO_2) fully suppresses the coupling reaction.

The possibility of the intramolecular coupling of aryl radicals has also been observed:

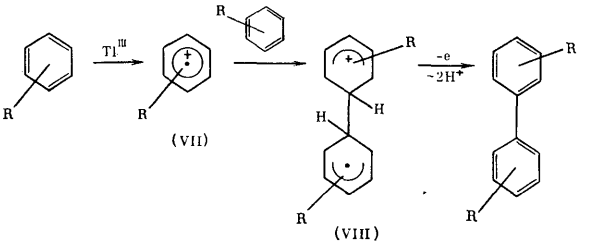


The authors put forward the hypothesis that the coupling of the aryl fragments proceeds via the intermediate formation of an aromatic radical-cation Ar^+. Data[10,11] indicating the intermediate formation of radical-cations in aromatic thallation reactions and also the formation of heptamethyldiphenylmethane (15%) in the interaction of TTFA with durene were quoted in support of this hypothesis. It is known that heptamethyldiphenylmethane is the product of the electrochemical oxidation of durene which proceeds via the intermediate formation of an aromatic radical-cation.[80]

The mechanism of the coupling of arenes on treatment with TTFA and the subsequent synthetic use of this method have been investigated in a study[81] in which five main procedures for the coupling of arenes are proposed: (1) $Tl(OCOCF_3)_3$, CCl_4, $BF_3.OEt_2$, room temperature; (2) $Tl(OCOCF_3)_3$, CCl_4, $BF_3.OEt_2$, −40–60 °C; (3) $Tl(OCOCF_3)_3$, CH_3CN, $BF_3.OEt_2$, room temperature; (4) $Tl(OCOCF_3)_3$, CF_3COOH, room temperature; (5) Tl.$(OCOCF_3)_3$, CF_3COOH, $BF_3.OEt$, room temperature. The addition of boron trifluoride etherate influences significantly the reactions in organic solvents such as CCl_4 and acetonitrile, since in their absence the coupling cannot be achieved in solvents of this kind.

The authors propose the following reaction mechanism: in the first stage an electron is transferred from the arene to TTFA with formation of the aromatic radical-cation (VII), which is followed by the electrophilic attack on the aromatic substrate by the radical-cation with formation of the intermediate (VIII), the oxidative aromatisation of which affords the biaryl (Scheme 13):

Scheme 13

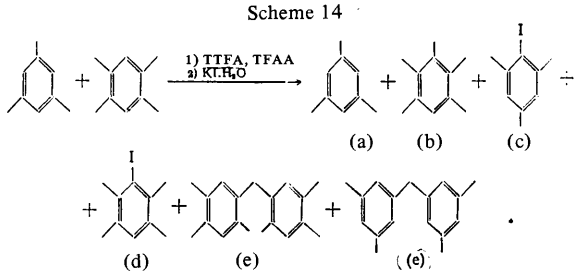


An an alternative, one can postulate that the coupling proceeds via the intermediate formation of an arylthallium compound.

The authors quote the following convincing arguments in support of the proposed mechanism:[81] (1) mesitylene and durene interact with TTFA in CF_3COOH both in the presence of added $BF_3.OEt_2$

and in its absence, but in the former case the aromatic ring is thallated while in the latter coupling leading to biaryl occurs; (2) if the biarylthallium bis(trifluoroacetate) is an intermediate in the biaryl formation reaction, one would expect that the reactivity of the arene in relation to $Tl(OCOCF_3)_3$ is determined by its basicity, whereas if the formation of the biaryl involves a one-electron transfer stage, then the factor determining the interaction of the substrate with the metal salt should be its ionisation potential. Mesitylene is a 200 times stronger base than durene but, in the competitive interaction of mesitylene and durene with TTFA, mainly the durene coupling products are formed (Scheme 14). The data in Scheme 14 are consistent with the difference between the ionisation potentials (8.4 and 8.03 eV) and also between the half-wave polarographic reduction potentials (1.85 and 1.59 eV) for durene and mesitylene respectively.

Scheme 14



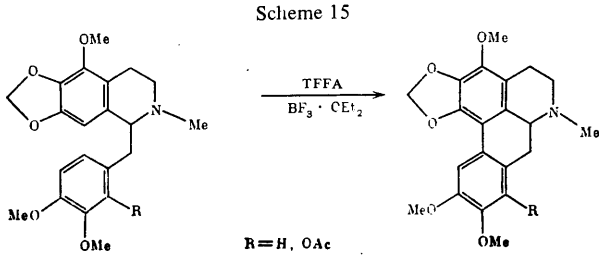
Reaction time	Yield of products, % a	b	c	d	e	f
1 h*	25.0	33.5	19.0	8.4	13.5	0.3
1 min**	38.1	52.0	0.3	0	8.5	0.1
1 h**	36.1	52.0	0	0	11.5	0.1

*Without $BF_3.OEt$. **With added $BF_3.OEt_2$.

The salts of other metals capable of accepting an electron, such as mercury(II) trifluoroacetate, iron(III) chloride, lead tetra-acetate, and $CoCF_3$, have been investigated in arene coupling reactions,[81] but the yields of biaryls obtained using them are lower than in the case where thallium(III) trifluoroacetate is employed.

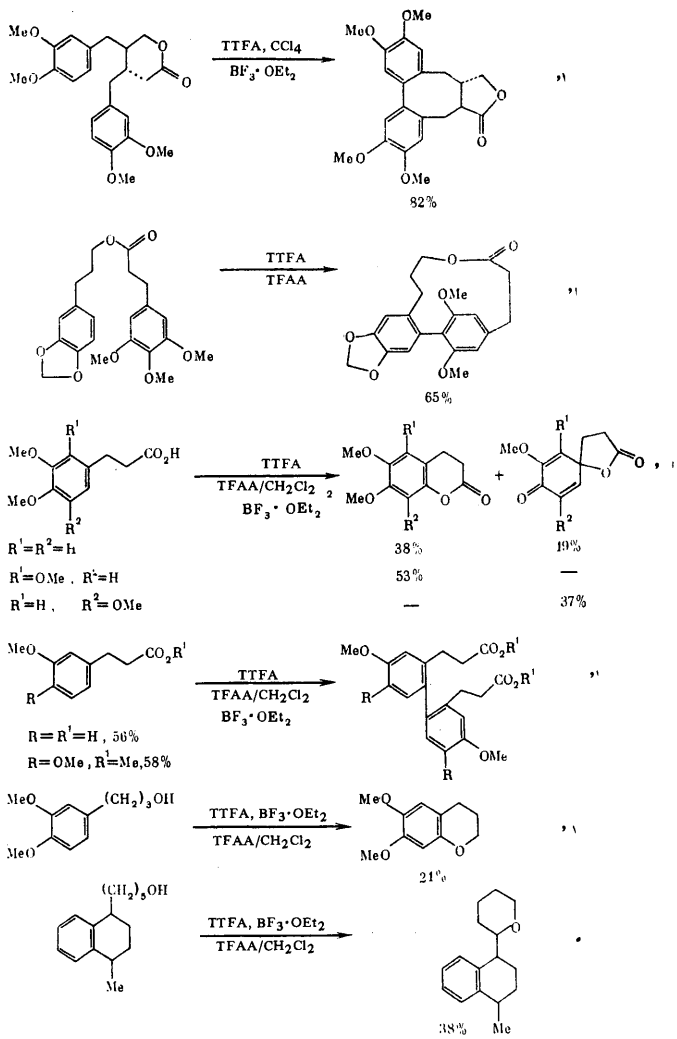
Although a C—Tl bond is in all probability not formed in the reactions involving the coupling of aryl groups on treatment with TTFA in the presence of boron trifluoride etherate, we believe it is essential to consider them briefly bearing in mind the extensive synthetic possibilities arising when this system is used. Thus, a whole series of alkaloids of the aporphine and homoaporphine series have been synthesised using the method developed by McKillop et al.:[79] (±)-ocoteine, (±)-*N*-acetyl-3-methoxynornantenine, (±)-kreysigine, (±)-*O*-methylkreysigine, and (±)-multifloramine.[82] The reactions were carried out in CH_2Cl_2 containing added $BF_3.OEt_2$: the product yields were about 50%. Scheme 15 illustrates the synthesis of (±)-ocoteine (R = H) and (±)-acetoxyocoxylonine (R = OAc) in 46 and 35% yields respectively.

Scheme 15



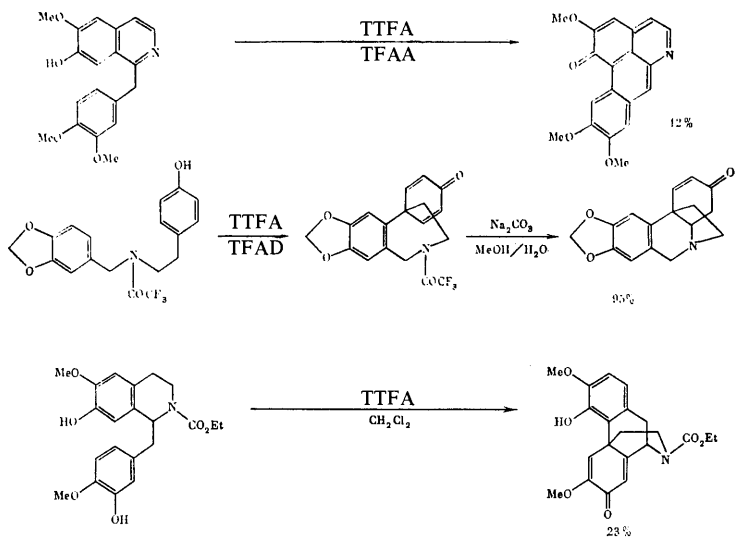
The single step synthesis of (±)-ocoteine developed by Taylor et al.[82] is simpler and the product yields are higher than in the method used previously.[83] Intramolecular cyclisation on treatment with TTFA has been used successfully for the synthesis of tetracyclic dibenzocyclo-octadiene systems[84] and also 11-and 13-membered cyclic lactones[85] (Scheme 16).

Scheme 16

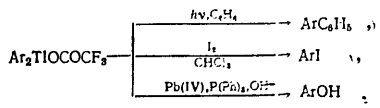


In those cases where the intramolecular coupling of the aryl fragments is impossible, the radical-cation intermediate is stabilised by the side chain or as a result of the reaction with another substrate molecule (Scheme 16). The intramolecular coupling of aromatic substrates on treatment with TTFA makes it possible to synthesise a whole series of polyarylene and spirocyclic compounds,[88–92] including certain alkaloids of the morphine series[93–95] (Scheme 17).

Scheme 17



Diarylthallium compounds can be used in organic synthesis for the preparation of asymmetric biaryls, aryl iodides, and phenols:[31]



The yields of the products are high, but the use of monoarylthallium compounds for the synthesis of biaryls, aryl iodides, and phenols appears more convenient.

Derivatives of monoarylthallium $ArTlX_2$ are the most promising and convenient starting compounds for organic synthesis. The use of diaryl- and triaryl-thallium compounds is evidently more useful in organometallic synthesis, as has been described, for example, in a monograph[28] and in two communications.[96,97]

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The Anomalies of the Increase in Viscosity in Binary Polymer Systems

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The literature data on the anomalies in the rheological properties of binary polymer systems, expressed as the increase in their viscosity characteristics, are examined and surveyed in the present review. The known hypotheses and theories of the anomalous changes in viscosity are analysed and an attempt is made to relate the concentration and temperature variations of the viscosities of binary polymer blends to their phase organisation.
The bibliography includes 94 references.

CONTENTS

I. Introduction 1069
II. Experimental observations of the anomalous increase in viscosity 1069
III. Hypotheses and theories of the anomalous changes in viscosity 1073
IV. Comparison of theory with experiment 1076

I. INTRODUCTION

The deviation of the characteristic features of the flow of solutions and melts from the behaviour of Newtonian liquids has come to be called an anomaly in viscosity.[1] However, according to Frenkel'[2] and Bartenev,[3] the natural manifestation in polymer systems of the strong intermolecular interaction, which determines the dependence of viscosity η on the stress τ and the rate of shear $\dot{\gamma}$, should hardly be classified as an anomalous phenomenon.

In the present review by "anomalies" we understand experimental manifestations of the viscosity-dependent properties which cannot be explained on the basis of the generally accepted theories of the flow of polymers and their blends.[1-13] From this point of view, the abrupt decrease or increase in the viscosity of polymers in the presence of low-molecular-weight, oligomeric, and polymeric additives should be classified as anomalies in the first place (see, for example, Refs.14-19). Cases where the viscosity of the mixture can prove to be lower or higher than the viscosity of the least or most viscous component of the system are of special interest.

The anomalous decrease in the viscosity of binary polymer systems† (BPS) has been discussed in detail in recent years in the review literature,[7,8,12,13] whereas virtually no attention has been devoted to the anomalous increase in viscosity (AIV). The illogicality of the phenomenon itself, namely the increase in the viscosity of the mixture after the introduction of a less viscous component,‡ and the absence of clear grounds for its theoretical justification have aroused a certain scepticism among investigators.

This review gives a systematic account of the experimental and theoretical results concerning the anomalous increase in the viscosity characteristics of BPS.

II. EXPERIMENTAL OBSERVATIONS OF THE ANOMALOUS INCREASE IN VISCOSITY

Publications concerning special studies of the AIV in BPS began to appear comparatively recently[14,15,17] although experimental observations of this phenomenon date back to studies as early as the 1960s.[16,18,20] The anomalies associated with the increase in the viscosity of the mixture compared with that of the highly viscous component itself are known not only for polymeric but also for low-molecular-weight organic[24,25] and metallic[26,27] liquids.

1. Mixtures of Low-molecular-weight Liquids

The increase in shear viscosity in a definite concentration range in a water-benzene mixture was observed as early as the beginning of the century. The dynamic properties[28-31] and anomalies in the viscosities[24,25] of a whole series of binary liquids systems have now been investigated. We may note two factors. Firstly, the increase in the viscosity of low-molecular-weight mixtures has usually been observed within a comparatively narrow range of compositions at temperatures close to the critical point. Secondly, the specific viscosity increments

$$\Delta\eta = \eta_m - \eta_v, \quad (1)$$

where η_m is the viscosity of the mixture and η_v the viscosity of the most viscous component, quoted in different studies, frequently do not agree since $\Delta\eta$ depends greatly on the experimental conditions.[30,31]

2. Mixtures of Metallic Liquids

The characteristic features of the dynamic properties of melts of metallic mixtures have been analysed in detail.[26] The extrema observed[26,27,32-36] on the viscosity isotherms for iron-nickel melts

† Unless specially stipulated, here and henceforth the binary polymer systems are understood as polymer-solvent mixtures, where the solvent can be a low-molecular-weight, oligomeric, or a high-molecular-weight compound.

‡ In terms of formal characteristics (but by no means in terms of the essential physical features), the effect discussed is close to the antiplasticisation phenomenon: the increase in the modulus and strength of polymers after the introduction of small amounts of plasticisers into the latter[21]—a phenomenon which aroused vigorous discussion in its time.[22,23]

as well as the anomalous effects consisting in the fact that, on heating in the temperature range from 1400° to 1800 °C, the viscosity η initially diminishes steadily as the temperature rises and then increases abruptly within a comparatively narrow temperature range (at 1500–1550 °C or at 1700–1750 °C [27,36]) only to fall again on raising the temperature still further are of greatest interest. According to Baum,[26] the previous history of the melt not only influences the intensity of the extrema but also determines the very fact of their existence.

3. Polymeric Liquids

The anomalous increase in viscosity has been observed in BPS of different types: mixtures of polymers with low-molecular-weight liquids[18,37] or with oligomers[15,38] and in blends of high-molecular-weight components.[5–8,14,16,17,39–42] In the last case the AIV effect has been observed for blends of two elastomers,[14,16,17,41] two plastics,[39,40,42] a plastic–raw rubber blend,[7,8,12,41] and also for block copolymers.[43,44] An extremum in the dependence of the viscosity on composition has been discovered both for binary polymer melts and for their solutions in a common solvent.[12]

The range of compositions in which AIV can be manifested is unusually broad. An increase in viscosity has been observed at both low concentrations (0.05–3%) of any of the components added to the system[7,11,12,15] and in the range of average compositions.[6,8,14,39] The range of concentrations in which the anomaly is manifested in the viscosity increment can be very narrow (fractions per cent) [15,18] or fairly broad (tens per cent).[14,39] Viscosity isotherms with a single extremum are characteristic of some systems,[12,16,38,39] while others have isotherms with two extrema[8,11,40] and in some instances there may be several extrema.[8]

It is so far impossible to compare quantitatively the published data on the AIV even for isotypical systems, since in most studies the viscosity parameters of the BPS have been determined on apparatus of different types and have been expressed in terms of different characteristics (effective viscosity, initial Newtonian viscosity, Mooney viscosity, torsional moment on the plastograph roller, the melt index, etc.).[12,14–17,37–42]

Analysis of the published experimental data shows that the sign of the extremum on the concentration variations of the viscosity, its absolute magnitude, and its position on the "viscosity–composition" curve depend on the molecular characteristics of the components, the temperature of the test,§ the deformation conditions ($\dot{\gamma}$ and τ), the method of preparation of the specimens, etc. A change in the parameters enumerated can lead not only to a displacement of the positions of the extrema or to a change in their absolute magnitude but can actually result in a transformation of a minimum into a maximum and conversely.

As an example, Fig.1 presents thermograms of the viscosity characteristic F (the force required to drive a melt through a capillary) obtained for a mixture of natural rubber (NR) and polybutadiene (PB) over the entire range of compositions at different shear velocities.[17] In the range of $\dot{\gamma}$ from 0.3 to 3 s^{-1}, the usual deviation of the viscosity[3,4,7] from additive values is observed but at higher shear velocities anomalies appear on the curves (the anomalies are shown shaded in the figure). In the given experiment, the character of the variation of F with mixture composition changes several times as $\dot{\gamma}$ is varied by five orders of magnitude.

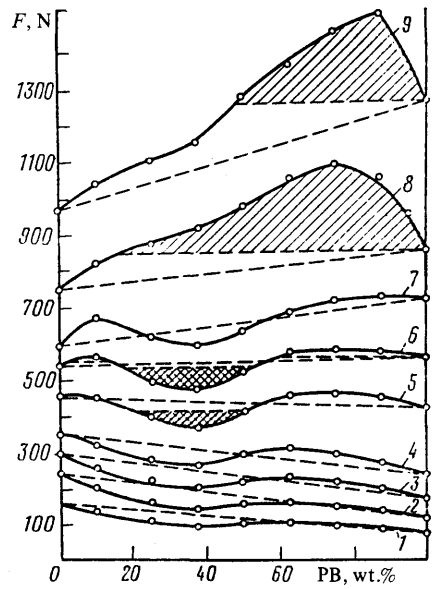


Figure 1. Dependence of the quantity F for the melt of a mixture of a natural rubber and PB on composition for different shear velocities ($\dot{\gamma}$, s^{-1}):[17] 1) 0.3; 2) 0.75; 3) 1.5; 4) 3.0; 5) 7.5; 6) 15; 7) 30; 8) 300; 9) 3000; T = 126 °C.

In the study quoted, it is emphasised that other measured viscosity parameters (for example, the Mooney viscosity at 100 °C and the twisting moment on the roller of the Brabender plastograph at 94 °C) do not exhibit significant anomalous deviations. Nevertheless, it follows from two investigations[14,16] that the AIV effect is not associated with any specific way of measuring viscosity.¶ Indeed, the viscosity maximum has been observed for the same mixture of NR and PB in a study[16] of the dependence of the parameter of the

§ In this case we are concerned not with the trivial influence of temperature, whose alteration can lead to fusion, devitrification, and the corresponding abrupt alteration of the properties of the system (such cases have been examined[45]), but with more complex mechanism of the effect of temperature on viscosity.

¶ Cases are known[6] where a change in the method of specifying the shear deformation or the design of the capillary in the rheological apparatus leads to the degeneration of the maximum to a minimum on the viscosity–concentration curve. As will be clear from the subsequent exposition, if the AIV is an objective property of a given system, then, regardless of the apparatus used, this effect can be observed by selecting the necessary experimental conditions for this purpose. Furthermore, the experimentally observed increase in viscosity can be a result of hydrodynamic flow effects determined by the design of the apparatus.

twisting moment on mixture composition. However, it is noteworthy that the experimental conditions in the study by Hess et al.[16] were different from those used by Folt and Smith.[17]

Using a capillary viscometer for the study of blends of polyethylene (HPPE) and polystyrene (PS), Han and Kim[14] observed, in particular, that, although at all the temperatures investigated (200°, 220°, and 240 °C) the viscosity thermograms have the form of curves with an extremum, nevertheless anomalies (in the sense adopted in the present review) are manifested at different temperatures and for different shear stresses in different ways.

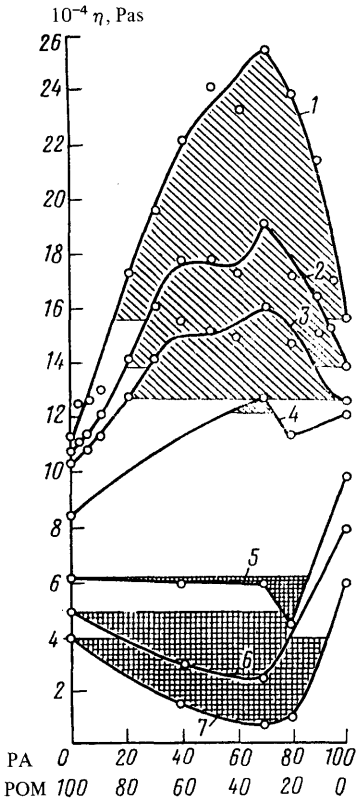


Figure 2. Dependence of the viscosities of POM–PA melts on composition at 190 °C and different shear stresses (10^4 τ, Pa):[47] 1) 1.27; 2) 3.93; 3) 5.44; 4) 6.30; 5) 12.59; 6) 19.25; 7) 31.62.

The influence of the shear stess on the AIV was also observed by Vinogradov and co-workers[39,40,46,47] in a study of the rheological properties of blends of polyoxymethylene (POM) and polyamide (PA) at 190 °C (Fig.2). With increase in τ from 0.6 to 3.5 × 10^4 Pa, Δη gradually diminishes in the range of compositions where a viscosity increment is manifested. Furthermore, after the attainment of a specific value of τ, the increase in η is replaced by its anomalous decrease, which progresses with increasing shear stress.

The examples presented show that the very fact of the anomalous variation of the viscosity of polymer blends compared with the viscosities of the components and the sign of this variation depend on the deformation conditions. The influence of the temperature of the test is just as complex. Apart from the study already mentioned,[14] this is indicated also by Lipatov's experimental data.[8] From the latter, it follows, in particular, that, when the composition of the polyethylene (HPPE)–polypropylene (PP) blend is altered, the viscosity of the melts, measured at 190–210 °C, passes twice through a maximum. An increase in the temperature of the test to 230–270 °C results in the disappearance of these maxima. In contrast to the case considered, in the cellulose acetobutyrate (CAB)–POM system (Ref.8, p.250) the AIV disappears on reducing the temperature and not on raising it.

In discussing the influence of temperature on the AIV, one should note several further unusual examples of an extremum in the variation of the viscosity.[7,12,13,16,18,21,41,42,45–50] A maximum has been observed[18] on the curve characterising the temperature variation of the viscosity of a solution of polystyrene in cyclohexane. This maximum can be recorded experimentally only when the temperature is varied in steps not greater than 0.2 K.

Data have been presented in a monograph[13] from which it follows that, after a monotonic decrease of the relative viscosity of an aqueous methylcellulose solution with increase in temperature, there is an abrupt increase in the range 50–55 °C.

It was shown in a recently published study[50] that η of a poly(vinyl chloride) (PVC)–trioxyethylene dimethacrylate mixture increases by a factor of two when the temperature is raised from 60° to 100 °C and then falls, reaching its initial value at 140 °C.

The maximum in the concentration variation of the effective activation energy for the viscous flow of BPS has been noted in several studies.[7,22,48,49]

Many investigators point out the role of the previous history of the system, which determines in many instances the character of the viscosity-dependent properties of BPS.[5–8,22,23,40,41,46] It has been specially emphasised[40] that, when POM is blended with PA in an alcoholic suspension (with subsequent removal of alcohol), there are two maxima on the "viscosity–composition" curve, but after the "dry blending" of the powders there is only maximum.

It has been shown[41] that a specimen prepared from PB–polyisoprene (PI) solutions is characterised by a viscosity maximum, which is converted into a minimum if the specimens are obtained by blending these raw rubbers on rollers.

The role of the previous history of the system as regards temperature has been noted.[7] If a mixture of PI and PS solutions is prepared and tested at a constant temperature (20 °C), then there is a viscosity maximum on the "property–composition" curve, but, when the system is first heated to 80 °C and then cooled to the temperature of the test (20 °C), a viscosity minimum is observed in the same composition range. This difference in behaviour is characteristic only of systems with a narrow molecular weight distribution (MWD) of the components. If the polymers constituting the blend were polydisperse, only a viscosity minimum was observed experimentally regardless of the previous heat treatment.

Some of the results discussed above indicate indirectly the kinetic nature of the anomalies discussed, but the communications quoted present facts indicating the thermodynamic nature of the anomalous

properties. Naturally, the hydrodynamic flow effects, associated with the structure of the blend, the design of the apparatus, and the deformation conditions, may mask or, on the contrary, can reveal anomalies which are objectively characteristic of specific systems.

4. Raw Rubber–Oligomer Mixtures

In the study of raw rubber oligoacrylate ester (OAE) systems,[15,28,51-58] the AIV was observed only in the range of low concentrations of the oligomers. It follows from the inspection of the flow curves for polydisperse SKI-3 raw rubber and its blends with two types of OAE—linear and branched[53]—that the AIV is manifested only in BPS with microamounts (< 0.5%) of the added linear oligomer. An increase in the OAE concentration to 1% restricts the range of τ values in which the anomalous effect is manifested and, on further increase in the oligomer content, the anomalies disappear over the entire range of τ.

It has been shown[51-53] that the AIV in binary raw rubber–OAE blends is not associated with the methodological characteristic features of the experiment and the chemical interaction of the components but is determined by the very structure of these systems, which depends on the nature of the components and their ratio.

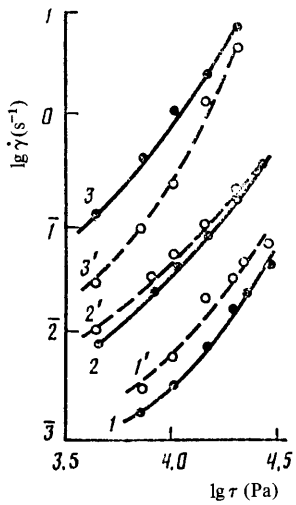


Figure 3. Flow curves for *cis*-polyisoprenes with MW = 6.2×10^5, 2.7×10^5, and 5×10^4 (curves 1–3 respectively) and their mixtures with 0.1 wt.% of TGM-3 (curves 1′–3′) at 70 °C.[54]

The relation between the anomalies in the viscosity-dependent properties of BPS on the molecular characteristics of the polymer component has been investigated.[54] Fig.3 presents the flow curves for *cis*-polyisoprene specimens differing in the molecular weight (MW) and their blends with trioxyethylene $\alpha\omega$-dimethacrylate (TGM-3), while Fig.4 presents the dependence of $\Delta \lg \eta$ for these blends on the MW of the polymer at different temperatures and shear stresses. It follows from these data that under the conditions selected for the test, the AIV effect is manifested only for blends of the low-molecular-weight raw rubber and OAE. With increase in the MW of the raw rubber, the relative magnitude of this effect diminishes and OAE has only a plasticising effect on high-molecular-weight raw rubbers.

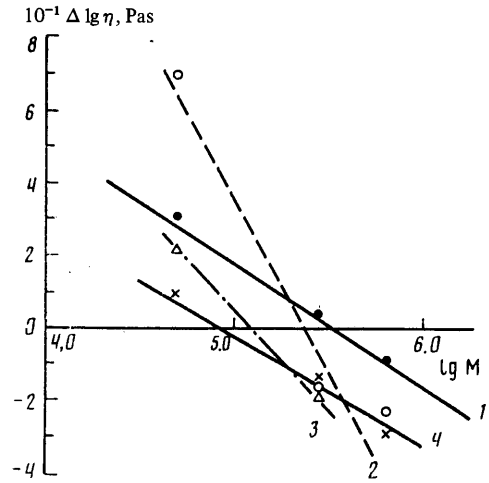


Figure 4. Dependence of $\Delta \lg \eta$ on the MW of *cis*-polyisoprene and its mixture with 0.1% of TGM-3 at 50 °C (curves 1, 3, and 4) and 70 °C (curve 2); $\lg \tau$ (Pa): 1) and 2) 4.0; 3) 3 and 6; 4) 4.26.[54]

It has been shown[54] that the influence of the shear stress in experiments with a low-molecular-weight raw rubber is analogous to that observed[52] for blends of industrial high-molecular-weight raw rubbers with OAE: an increase in τ lowers the relative magnitude of the viscosity increment. On the other hand, the effect of temperature proved to be different. In contrast to experiments with industrial SKI-3 and SKD raw rubbers,[38,51,52] where the viscosity increment was totally eliminated with increase in temperature, in the given instance the relative magnitude of the AIV effect depends not only on the tendency towards a change in temperature and τ but also on their ratio: for some shear stresses, $\Delta\eta$ increases with increase in temperature whilst for others it diminishes. Nor can a distinct $\Delta\eta = f(c)$ relation be traced for blends of low-molecular-weight raw rubbers with OAE. It has been shown[54] that this is a consequence of the random variation of the MWD of raw rubbers in different syntheses.

An analogous conclusion has also been reached in a study[59] where it was shown in relation to blends of two polydisperse polymers (HPPE and POM) that the AIV depends in many respects on the MWD of the components and that the extremum is gradually abolished as the low-molecular-weight fractions are removed.

In the analysis of the influence of the polymeric component on the character of the manifestation of viscosity anomalies in raw rubber–OAE systems, attention should be drawn to two factors. (1) The viscosity anomaly is manifested most clearly and logically only in BPS based on polydisperse raw rubbers;[52] (2) even a slight difference between the MW and MWD of industrial batches of raw

rubbers may result in a situation where the AIV, which is consistently reproduced in specimens prepared from the same batch of raw rubber, cannot be observed in specimens obtained from another batch.[51-54]

The ambiguity of the entire set of experimental observations of the anomalous variation of the viscosity of BPS of different types considered above indicates the existence of parameters of the system (the actual system and not its components) which were not taken into account by the investigators and which can in fact be responsible for the extrema on plots reflecting the dependence of the viscosity of the BPS on concentration and temperature.

III. HYPOTHESES AND THEORIES OF THE ANOMALOUS CHANGES IN VISCOSITY

1. Low-molecular-weight Liquids

Ostwald[60] was apparently the first to suggest a relation between the increase in viscosity through an extremum and the phase transition in the vicinity of the critical point. This hypothesis was based on the modelling of the structure of the system in the critical state by "particles" constituting small-scale inhomogeneities, which led to an analogy with highly disperse colloids whose viscosity is higher than that of the solutions. This "colloidal" model was used for a comparatively long time to interpret many experimental observations at a qualitative level (see, for example, Refs.24, 25, and 28–31).

Quantitative schemes relating the shear viscosities of liquid systems to the appearance of large-scale fluctuations near the critical point began to appear in the 1960s. A theoretical justification of the anomalous variation of viscosity and other transport coefficients in mixtures of low-molecular-weight liquids in the critical state was initially provided by Fixman's studies,[61,62] concerned with the hydrodynamic description of the macroscopic properties of these mixtures within the framework of the approximation of interacting modes, and later by studies[63-65] in which this idea was examined within the framework of the decoupled-mode and the dynamic renorm group approximation.

The physical significance of all these approaches is that, when the system exists in the critical range of compositions and temperatures (c_{cr} and T_{cr}), then part of the mechanical energy (for example, in the deformation of the mixture) is dissipated on long-wavelength concentration fluctuations at a consequence of the interaction of the latter with the velocity gradient and their diffusion-dependent dissipation. Hence it follows naturally that the viscosity of the mixture in the critical state should increase, because in this case the entire shear energy is not consumed on the displacement of the molecules.

Thus, for systems in the vicinity of the critical point, the experimental viscosity η_m consists of the regular ("non critical") component η_r, which has been identified with the viscosity of the homogeneous solution, and the excess ("critical") correction ($\Delta\eta_{cr}$), whose value depends on the closeness of the experimental conditions to the critical conditions for the given system:

$$\eta_m = \eta_r + \Delta\eta_{cr}, \quad (2)$$

$$\Delta\eta_{cr} = f(r^{\Phi}), \quad (3)$$

where $r = (T - T_{cr})/T_{cr}$ is the critical parameter of the shear viscosity.

Solutions of the hydrodynamic equations within the framework of the approximations mentioned above yield in some cases[61-63] identical values of the parameter Φ, whilst in others[63-66] they lead to non-concordant results.

The ideology of large-scale fluctuations is applicable to systems which are both at the critical point and in the region of metastable states near the spinodal curve. The long-wavelength fluctuations arising under these conditions have the same influence on the shear viscosity.

Comparison of the experimental and calculated (within the framework of dynamic scaling) data[67,68] shows that Φ varies within broad limits: from −0.37 to 0.5 not only for different systems but even for isotypical systems.

2. Metallic Liquids

Virtually all the explanations of the concentration-dependent anomalies in the viscosities of metallic liquids are based on the use of the cybotactic model of the structure of liquids.[26,27]

Two versions of the possible explanation have been considered.[26] In one of them, it is assumed that the introduction of an additive or an increase in temperature lead to the decomposition of the initial large cybotaxes and to the formation of new ones having a smaller store of internal energy than the initial ones, which in fact causes an increase in the viscosity of the system. In the other version, the rearrangement of the structure of the cybotaxes is associated with the change in composition or temperature regarded as an activated process with a transition state, whose appearance requires an expenditure of additional energy. The entropy of the transition state is higher than that of the initial or final state and the change in the entropy of activation for viscous flow in the transition state accordingly proves to be smaller, while the activation energy and the viscosity are higher.

Unfortunately all the treatments of the anomalies in the viscosity-dependent properties of metallic melts are qualitative.

3. Polymeric Liquids

The AIV effect has been hardly considered in the reviews published in recent years on studies of the viscosities of dilute and concentrated solutions of polymers and polymer melts.[69,70] In the original studies the most varied ideas and approaches have been invoked to account for the anomalous variation of the viscosity-dependent properties of BPS, but all of them (with some exceptions—for example in Refs.5, 40, and 56) had as their aim the explanation of the causes of the abrupt decrease in viscosity. Ideas involving structural plasticisation,[23,46,71] a change in the free volume of the system after the introduction of the second component,[4,8,42] a decrease in the energy of the intermolecular interaction in the presence of the additive,[7,12] the separation into layers comprising different phases,[5-8] critical[7] and metastable[8,11] states of the system, etc. were invoked for this purpose. The development of these ideas has been reflected in reviews and monographs[7,8,11,12] and they will therefore not be considered in the present communication. We shall only mention that, from our point of view, the approaches based on the search for correlations between the anomalies in the rheological properties and the system thermodynamics proved most fruitful and most general.[7,8]

Judging from the number and wide variety of the experimental facts (see Section II), the AIV effect in BPS is a fairly common phenomenon. However, a reasonable explanation, providing for a single treatment of all the characteristics of its manifestation, has not so far been found. In many instances the causes of the increase in the viscosity of BPS are so evident that the absence of this effect would have to be regarded as anomalous and not its experimental manifestation. Thus, the increase in the viscosity of the blend of powdered PVC with liquid OAE mentioned above[50] with increase in temperature must inevitably occur as a consequence of the conversion of the mixture into a monolithic form and the transition from the flow of a dispersion to the flow of a plastisol. Gel formation in a solution of methylcellulose, occurring at a specific concentration of the solution in a specific temperature range, should also entail an increase in viscosity, which has in fact been observed in the experiment discussed above.[13] On the other hand, the disappearance of one of the two viscosity maxima, noted in a study[40] of the POM–PA system on raising the temperature, should have occurred without the fusion of the crystallising component.

It is just as evident that the phase transitions in BPS causing the transformation of the flow of single-phase solutions into the flow of dispersions can lead to an increase in viscosity, for example, in conformity with the familiar Einstein equation:†

$$\eta_m = \eta_0(1+2{,}5\varphi), \qquad (4)$$

where η_0 is the viscosity of the dispersion medium and φ the volume fraction of the disperse phase. However, from this it does not follow by any means that the viscosity of the mixture must be higher than the viscosity of the disperse phase.

(a) Single-phase BPS

A large group of studies,[2,4,7,13,73] devoted to the characteristics of the flow of polymer solutions, were confined to the elucidation of the possible causes of the deviation of the viscosities of the BPS from additivity without concentrating attention on the anomalously high values of these deviations. For this purpose, the idea that the free volume of the system changes (increases or decreases) on mixing the initial components were resorted to; the idea of a fluctuating network of entanglements, which can be more or less stable in BPS than the initial polymers, has also been used. In some cases, the concept of the supermolecular structure of polymers in solutions has likewise been employed.[4]

Virtually all the experimental features observed for polymer solutions can be ultimately accounted for qualitatively within the framework of the kinetic theory of Frenkel' or its modifications.[10]

Application of the scaling hypothesis to the analysis of the dynamic properties of polymer solutions made it possible to[74,75] impart to the idea of entanglements the form of quantitative relations. In particular, the viscosity of solutions of flexible-chain polymers is described by the expression[74]

$$\eta_m \simeq \eta_s N_e^{-2} N^3 \varphi^{\frac{3}{3\nu-1}} = \eta_s N_e N^3 \varphi^{11/4}, \qquad (5)$$

where η_s is the viscosity of the solvent, N the number of monomer units in the polymer chain, N_e the average length of the chain between entanglements in the polymer melt, φ the volume fraction of the polymer, and $\nu = 3/5$ the swelling index of the coils in semidilute solutions.

This approach is being vigorously developed at the present time. For example, different scaling expressions have been obtained recently[76] for the viscosities of systems of polymer solutions in each of the six regions of a dynamic phase diagram (Fig.5) as a function of the solution concentration φ, the length of the polymer chain N, and its flexibility P.

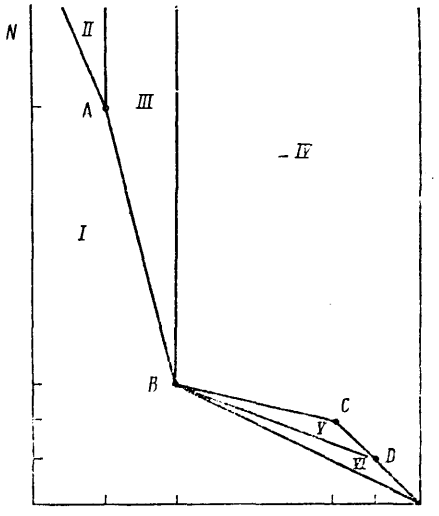


Figure 5. Dynamic phase diagram for a BPS solution;[76] φ = volume fraction of the polymer; points A, B, C, and D correspond to P^3, P, $P^{3/4}$ and $P^{1/2}$ respectively.

In region I, the entanglements between the macromolecular coils are insignificant and the viscosities of the solution in the solvent are identical. With increase in φ, the swollen coils begin to overlap and the system passes to region II, and there is a corresponding change in the laws governing viscous flow. The subsequent differentiation of the regions in the diagram is associated with allowance for N and P. For example, if $P = 1$, then the differences between the properties of the solutions corresponding to regions II–VI disappear, these regions "merge", and only two zones remain on the diagram—with overlapping and non-overlapping coils. On the other hand, if $P = 1$, then (and this is important for the problem discussed here) in each of the differentiated regions of the diagram the viscosity depends in different ways on φ. For example, at high dilutions ($\varphi_m \simeq \varphi^{3.8}$), the power exponent increases to 6 in the region of semidilute solutions and on passing to region V it diminishes to 1.4. This makes it possible to explain the presence of extrema on the $\eta_{sol} = f(\varphi)$ curves. Furthermore, the different power relations beween η_m and P, noted[76] for different regions of the diagram, and the temperature dependence of the flexibility of the molecule explain the non-linearity of η_m as a function of T. Analysis of the expressions quoted[76] shows that in region II the viscosity of the solution

† Subject to the condition that this equation, which was derived for dispersions of hard spheres, is applicable to BPS.[72]

should diminish on heating, while in region IV it should increase. Consequently, depending on the BPS concentration, an increase in temperature can lead to both an increase and a decrease in viscosity.

(b) Two-phase BPS

In order to account for viscosity-dependent properties of BPS known to be heterogeneous, two approaches are mainly used. In one of them the viscosity of the BPS is considered from the standpoint of the flow of colloidal dispersions for which the increase in viscosity with increasing fraction of the disperse phase is reasonable, and this is why a number of workers[5,7,11,22,23] have been surprised by the appearance of minima and not maxima on the $\eta_m = f(\varphi)$ curves.

For heterogeneous BPS, which can be regarded as dispersions with particles deformed under the influence of a load applied to the system (i.e. the shape of the particle is a function of τ and $\dot{\gamma}$), the applicability of Eqn.(4) is problematic (see the preceding footnote). There is as yet no universal theory of the flow of dispersions, although there are many empirical equations and models taking into account the influence of individual factors (the nature and shape of the particles, the state of aggregation of the disperse and dispersion phases, etc.). We may note, for example, the equation proposed by Lipatov,[11] which takes into account the molecular weight of the polymer, and the Schowalter–Taylor model[79] in which the viscosity of the mixture is related to the viscosity of each phase.

Thus the increase in viscosity is inherent in the very nature of the flow of colloidally disperse systems, although none of the known models lead to the conclusion that η_m should be greater than the viscosity of the most viscous component.

The second approach is based on the ideas concerning the structural transformations introduced by the BPS flow process itself, for example, the formation of a vibrous structure of the stream as a result of one of the components being stretched in the direction of the deformation or as a result of the formation of alternating annular layers when emulsions flow in a capillary,[7,14,39,40,77,78] etc. When the composition of the initial mixture, the deformation conditions, or the design of the apparatus are altered, the diameter of the fibres, the radius of curvature of the layers, the order in which they alternate, etc. can change. As a result of hydrodynamic effects, this can induce in its turn a decrease of an increase in the translational mobility of the macroscopic system as a whole.

(c) Binary Polymer Systems with Limited Compatibility of the Components

For systems of this type, the change in the character of the flow and all the non-linear effects in the concentration and temperature dependences of the viscosity are attributed to phase transitions, while anomalous deviations are usually attributed to the characteristic features of the structures formed under these conditions.

Thus the increase in viscosity has been explained[80] by the possibility of the formation of "strongly interlinked mosaic-like structures" during spinodal separation. In other studies,[51–55] the anomalous variations of the viscosity-dependent properties of rubber–oligomer systems are interpreted by analogy with the antiplasticisation effect.

Having compared the experimental $\eta = f(\varphi)$ curves with phase diagrams, Lipatov[8] proposed a modified Mooney's equation with a description of the viscosity of BPS in the region of a homogeneous state (before the attainment of the binodal curve):

$$\eta_m = K(1-\varphi_1)^{\alpha} M^{3,4}, \tag{6}$$

where K and α are empirical constants and φ_1 is the concentration of one of the polymers; in the region of the two-phase state (within the spinodal curve), Einstein's Equation (4) holds, while the viscosity of the system in the metastable zone (between the binodal and spinodal curves) can be calculated by means of the equation

$$\eta_m = K(1-\varphi_1')M^{3,4}(1+2{,}5\varphi_1''), \tag{7}$$

where $\varphi_1' + \varphi_1'' = \varphi_1$ represents the concentrations of the added polymer in the continuous and disperse phases and its overall content in the system.

Thus the section corresponding to a decrease in the viscosity on the $\eta = f(\varphi)$ curve is described by Eqn.(6), while the increase in viscosity is described initially by Eqn.(4) and then, after the interaction with the spinodal curve, by Eqn.(7).

Although the scheme considered does not yield quantitative agreement with experiment (as was pointed out by the author himself), nevertheless it permits a qualitative explanation of the possibility of the appearance of a viscosity minimum on the $\eta_m = f(\alpha)$ curves and the subsequent increase in viscosity. However, a whole series of other experimental facts (in particular the multiplicity of extrema) can in no way be accounted for by this scheme.

(d) Theory of the Viscosity of BPS in the Critical State

The work of Manevich and co-workers[81] is based on the fundamental idea of the approximation of interacting modes. However, in contrast to earlier studies,[61,62] they took into account additionally the non-Newtonian character of the flow of polymeric liquids and the asymmetry of the phase diagrams of polymer blends. As a result, the following expression was obtained for positive critical corrections to the viscosity:

$$\Delta\eta_{cr} = ac_2^2 \frac{1}{q} M^3 \left(1 + \frac{b}{q^4}\right), \tag{8}$$

where $q \simeq [(T - T_{cr})/T_{cr}]^{1/2}$, c_2 is the concentration of the polymer, M its molecular weight, and a and b are numerical coefficients. The parameter q is related in its turn to the chemical potential of the system μ_1 by the expression

$$\frac{4\pi a}{q^2} = \frac{V_1}{c_2}\left[KT \Big/ \left(\frac{\partial \mu_1}{\partial c_2}\right)_{P,T} + m\right], \tag{9}$$

where $m = V_2/V_1$ is the ratio of the molecular volumes of the components. The change in the chemical potential is calculated here in accordance with the Flory–Huggins theory.

It follows from the theory of the viscosity of BPS in the critical state, that, in order to record the increase in viscosity, it is necessary to select the temperature-concentration conditions in such a way that the temperature and concentration are either identical or approach T_{cr} and c_{cr}.

Unfortunately in the form presented by Manevich et al.,[81] this theory does not establish quantitative criteria which would make it possible to estimate the difference between the experimental parameters of state and the critical values for which the contribution of the critical corrections is comparable to the experimental accuracy. It is

qualitatively clear that, if $\Delta c = c_{cr} - c \to 0$ and $\Delta T = T_{cr} - T \to 0$, then $\eta_{cr} \to$ max. But for each specific polymer–solvent pair, the Δc and ΔT for which $\Delta\eta_{cr}$ is comparable to η_m apparently have values characteristic of the given system. This apparently also explains the finding that, in the study mentioned above,[18] the AIV could be observed only under conditions where the temperature was varied in steps $\Delta T \leqslant 0.2$ K.

We emphasise that, if the current values of c and T are less than the critical values, then their increase brings the system closer to the consolute temperature (CT), whereupon $\Delta\eta_{cr}$ increases, which means that η_m will also increase. On the other hand, if c and T are greater than the critical values, then the subsequent increase in these parameters will entail a decrease in $\Delta\eta_{cr}$. As already mentioned in the previous Section, significant changes in the character of the concentration and temperature dependence of the viscosity have indeed been observed for BPS investigated under different conditions. It also follows from the theory examined that, with increase in the shear stress, the large-scale concentration fluctuations, which determine the increase in viscosity, are gradually disrupted‡ with a corresponding decrease also in $\Delta\eta_{cr}$.

(e) Theory of the Viscosity of BPS Near the Limit of Thermodynamic Stability

The character of the variation of the viscosity of BPS as the spinodal curve is approached, where large-scale concentration fluctuations also arise spontaneously, has been examined.[82,83] When a shear deformation is superimposed, part of the energy of the hydrodynamic flow is dissipated at these fluctuations which in fact entails an increase in the viscosity of the blend. The addition ("spinodal") correction to the viscosity has the form

$$\Delta\eta_{sp} = \frac{3\sqrt{2}\pi^3}{20}\frac{\rho f^2 k_B T\,(N_A(1-c)\,\tau_M^A + N_B c\tau_M^B\,(N_A N_B)^{1/2}}{N_e[N_A c + N_B(1-c) - 2\chi c\,(1-c)\,N_A N_B]^{1/2}}, \qquad (10)$$

where c is the concentration of component A expressed in terms of the number of monomer units, N_A and N_B are the degrees of polymerisation of the components, τ_M^A and τ_M^B are the microscopic relaxation times of the components, N_e is the number of monomers between entanglements in the reptation diffusion model along the "tube" formed by the entanglements, f is the Onsager coefficient characterising the degree of the intermode relation between the viscous and diffusion modes, k_B is the Boltzmann constant, and χ is the Huggins constant.

Eqn.(10) reflects the dependence of $\Delta\eta_{sp}$ on the length of the molecular chains of the components, their relaxation characteristics, the degree of the intermode relation, and the composition, temperature, and density of the mixture. However, the applicability of this formula is limited to monodisperse systems. In order to account for the polydispersity of the macromolecules, an additional function of the distribution density with respect to the degrees of polymerisation of each component (Π_A and Π_B) was introduced[82] into Eqn.(10).

‡ A qualitative dependence of the microstructure of the blend on the shear stress has been described[2,84] and it has been shown that, with increase in τ, the dimensions of the microparticles and the formations produced by association diminish. The influence on τ on the orientational effects of concentration fluctuations, which induces the anisotropy of the dynamic properties of BPS, has been noted.[85]

Analysis of the integral form of the expression for $\Delta\eta_{sp}$ with allowance for Π_A and Π_B shows that, for a specified mixture composition and the total number of molecules in the system $N_A c + N_B(1-c)$, only those molecules contribute to $\Delta\eta_{sp}$ whose N_A and N_B for specified c and χ fall within the region adjoining the thermodynamic stability limit of the BPS. The same A and B molecules (for example, molecules with low degrees of polymerisation) which for a given T form true solutions with one another and those (for example, molecules with large N_A and N_B) which form heterogeneous mixtures under these conditions do not contribute to $\Delta\eta_{sp}$ and influence the macroscopic viscosity of the system only additively or in accordance with other laws.

Thus, if a "polydisperse" system with specified experimental c and T falls within the region adjoining the spinodal curve, then and only then do some of the molecules participate in the formation of large-scale fluctuations and only that fraction of them determines the agreement between the experimental viscosity and the value calculated by Eqn.(10). The remaining molecules, for which the elementary flow steps take place in accordance with other laws, will mask the flow in accordance with Eqn.(10).

The reliability of the experimental observation of the AIV has also been estimated.[82] For $\Pi_A \to 0$ and $\Pi_B \to 0$, the possibility of observing the effect is determined by the relation

$$\delta\eta/\Delta\eta_{sp} = \delta T/2\Delta T, \qquad (11)$$

where $\delta\eta$ is the accuracy of the measurement of $\Delta\eta_{sp}$ and δT is the accuracy of the thermostatic temperature control. Hence it follows that the possibility of obtaining a reliable value of $\Delta\eta_{sp}$ appears only if $\Delta T \geqslant \delta T$. It was found that, for a monodisperse BPS characterised by $N_A = N_B \simeq 10^4$, $N_e \simeq 10^2$, $\tau_M^A = \tau_M^B = 10^{-9}$ s, $f \simeq 1$, and $\rho \simeq 1000$ kg m^{-3}, an increase in viscosity by a factor of 2 (i.e. when $\Delta\eta_{sp} = \eta_r$) can be observed near the spinodal curve for $\delta T \simeq 1$ K.

The "critical" and "spinodal" corrections to viscosity have been revised[83] in connection with allowance for osmotic forces whose interaction with viscous friction forces is believed[74] to determine in many respects the mechanism of the dynamics of polymer solutions and melts.

The inclusion of the osmotic pressure of components A and B in the rheological equation for BPS leads to an expression in which, apart from positive corrections inducing an increase in viscosity, there is also another correction $\Delta\eta_{os}$ whose sign is negative (reducing the viscosity). This is due to the fact that osmotic forces facilitate the "dissipation" of the concentration fluctuations themselves and hence less of the energy supplied to the system from outside is expended on this process.

Yet another important conclusion has been made,[83] namely that the more significant the difference beween N_A and N_B, the greater the contribution by the above negative correction to the overall $\Delta\eta$. In other words, the greater the difference between the MW of the components of the BPS, the greater the probability of a decrease and not an increase in viscosity.

IV. COMPARISON OF THEORY WITH EXPERIMENT

The above analysis of experimental and theoretical data indicates a wide variety of possible causes leading to the AIV and the absence of a single view concerning the mechanism of this phenomenon. However, it is evident that the increase in the viscosity of BPS is always associated with structural features characteristic of them as mixed systems.

1. The Phase Diagram of BPS

Fig.6 presents a conventional phase diagram of BPS in terms of the variables $\varphi_A - T$, where φ_A is the concentration of the polymeric component. Regions have been differentiated in the diagram in which the laws governing flow are apparently different. The phase diagrams of BPS have been analysed in detail in a number of studies.[13,86–88] Here we shall note only the most general postulates necessary for further logical exposition. Fig.6 illustrates the θ-line for the solutions shown by a dashed curve. In the zone above the θ-line, only three regions are shown: with non-overlapping (V) and overlapping (V') coils as well as the region of swollen gels (V''), although in principle this zone can be differentiated in greater detail (as was done, for example, by Semenov[76]).

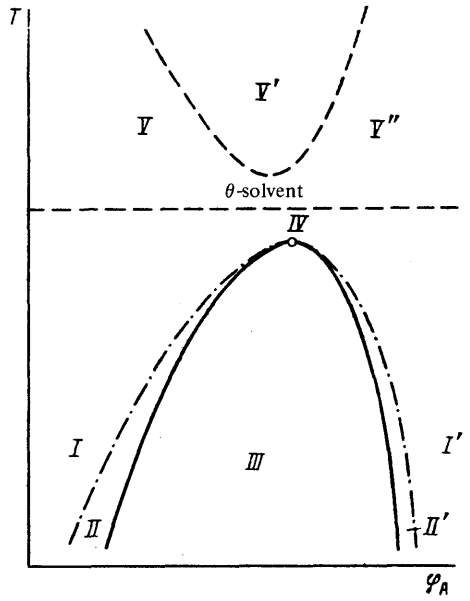


Figure 6. Conventional phase diagram for a BPS.[54]

In the zone of "poor" solvents (below the dashed line), six regions have been differentiated: two regions of true solutions—with an excess of the solvent (I) and with an excess of the polymer (I'); two regions of a metastable state (between the binodal and spinodal curves)—to the left (II) and to the right (II') of the spinodal curve; the region of two-phase states (III) located within the spinodal curve; the region of the critical state (IV) adjoining the upper consolute temperature (UCT).§ The positions of the branches of the binodal and spinodal curves depend on the affinity of the components (χ) and on their molecular-weight characteristics. For example, if N_B is large (the BPS consists of two polymers), then the branches are usually close to the coordinate axis and region (III) predominates in the diagram. If the MW of the solvent diminishes (transition to oligomeric and low-molecular-weight liquids), then the solution zone (especially to the left of the binodal curve as virtually all known phase diagrams of BPS are asymmetric) as a rule becomes broader.

Thus above the θ-line BPS form two solutions over the entire composition range regardless of temperature. Below the θ-line, two solutions are formed for any values of φ only at $T >$ UCT. On the other hand if $T <$ UCT, then BPS are by definition systems with limited compatibility, and when $\varphi < (\varphi'_A)_B$ (where the subscript B denotes the position of the point on the binodal curve) they form true solutions (region I) which correspond to traditional ideas about polymer solutions[4] whereas in the case where $\varphi > (\varphi''_A)_B$ they form solutions corresponding to molecularly plasticised systems.[22,23] Here $(\varphi'_A)_B$ and $(\varphi''_A)_B$ are the polymer concentrations along different branches of the binodal curve at a specified T.

Unfortunately few studies of the anomalies in the viscosity-dependent properties of systems with known phase diagrams have so far been published.[11,52,59,80] It is therefore difficult to compare experimental rheological data with thermodynamic features of the BPS. This is especially significant for systems with limited compatibility of the components for which the position of the CT and the regions of the metastable state are unknown in the vast majority of cases. As regards solutions and heterogeneous mixtures, there are usually sufficient indirect data confirming whether or not they belong to a particular phase organisation.

2. Solution Regions

The explanations of the causes of the non-linear effects of the AIV observed in polymer solutions and in single-phase BPS melts have not been adequately supported by arguments at the present time. The scaling approaches to the analysis of the dynamics of dilute and concentrated polymer solutions in "good" solvents (regions $V - V''$ in the diagram), which have been developing vigorously, undoubtedly contain new ideas capable of providing in the future a clear-cut physical interpretation of the entire set of effects which have been discovered. Examples of the fruitfulness of these approaches have been published.[74,76] However, in the present state of the development of these views, statistical physics has not yet provided a general picture of the relation between the viscosity and the parameters of state of BPS, the system thermodynamics, and the conditions of the rheological experiment. Nevertheless, it has yielded the very significant conclusion that the fundamental laws do not prohibit the possibility, in principle, of an increase in viscosity in polymer–solvent systems both in the region of dilute and semi-dilute solutions and in the region of polymer gels.

The scaling approaches being developed should undoubtedly influence also the development of the theory of polymer solutions in solvents with different thermodynamic affinities (regions I and I').

In our view, the approach based on the cybotactic (by analogy with metallic liquids) or anisotropic (by analogy with liquid crystal systems) models is undoubtedly promising. However, virtually no examples of the interpretation of the experimentally observed anomalies in the viscosity-dependent properties of BPS from these standpoints are encountered in the literature.

§ For systems with a lower consolute temperature (LCT), the above reasoning does not change fundamentally.

3. The Region of Two-phase BPS

The heterophase nature of BPS is as a rule due to the following causes: (1) the components are entirely thermodynamically incompatible; (2) the compatibility of the components is limited but at the experimental temperature the compositions of the systems investigated correspond to the two-phase state; (3) the components are potentially miscible but, by virtue of kinetic causes, the system has not attained equilibrium by the beginning of the rheological experiments and is therefore characterised by a definite level of heterogeneity; (4) phase separation takes place during the flow process. We shall examine further two main groups of factors which can lead to an anomalous variation of the viscosity-dependent properties regardless of the cause which has induced the heterophase nature of the BPS. One of them is associated with the intrinsic heterogeneity of the initial mixtures, which determines the characteristic features of their flow as disperse systems. The other is associated with the morphology of the extruded materials, arising solely during the flow process, which can alter the mechanism of mass transfer during the rheological experiment. It is more accurate to say that the structural changes accompanying the flow of BPS can mask the manifestation of features characteristic of classical dispersions.

As mentioned above, there is as yet no universal theory of the flow of polymer dispersions and the Einstein, Goot, Wand, Andrade-de Gusman, Mooney, Schowalter–Taylor, etc. equations are used to account for the experimental observations (depending on the form of the particles of the disperse phase and the range of concentrations of the dispersions). Within the framework of these ideas, the increase in the viscosity of BPS as a function of concentration is evident. However, a satisfactory explanation of the anomalously high values of $\Delta\eta$ observed experimentally has not yet been found.

As regards the factors inducing the increase in viscosity (or diminishing it) as a consequence of the change in the structure of the extruded material during the flow of BPS, at the present time they are considered only at the qualitative level. Examples were quoted above (see, for example, Refs.7, 39, 40, 47, 80) in which typical approaches to the interpretation of the anomalies in the increase and decrease in viscosity as the morphology of the extruded material varies are described.

We may note that it is precisely in two-phase BPS that the influence of the design of rheological apparatus on the results of the rheological experiment is manifested to the greatest extent. This is apparently associated with the fact that the method used to establish a given shear deformation, the design of the capillary, and hence the flow regimes in many respects determine the structure of the BPS formed during the flow process. For example, the transformation of the viscosity minimum into a maximum on the $\eta = f(c)$ curves, which has been observed[6] for a heterogeneous system as the length of the capillary was varied, is apparently induced by the increase in the viscosity of the wall layer, which is caused in its turn by a change in the hydrodynamics of the flow.

4. The Regions of the Metastable and Critical States

A distinctive feature of BPS with limited compatibility of the components is the fact that the structure of these systems, arising in the metastable and critical states itself, induces the manifestation of anomalies in dynamic properties. The large-scale fluctuations arising spontaneously in the critical region and in the vicinity of the spinodal curve, dissipate "non-productively" part of the energy of the shear deformation of the system, which leads ultimately to an increase in the macroscopic viscosity of such BPS.

Manevich and co-workers[81–83] were able to impart (in relation to BPS) the form of mathematically complete physical series to the idea of the dissipation of energy by large-scale fluctuations. The viscosity η_m, manifested in regions II, II′, and IV (Fig.6), consists of the viscosity of the regular solution (η_r) and the additional positive corrections $\Delta\eta_{sp}$ (regions II and II′) and $\Delta\eta_{cr}$ (region IV). Furthermore, it follows from the study of Mitlin and Manevich[83] that the "osmotic" correction, whose sign is negative, contributes to η_m. Each correction is defined by the corresponding equations, relating its value to the molecular characteristics of the components, the thermodynamic parameters of the system, the state parameters, and the deformation regimes.

Comparison of the conclusions derived from these theories with experiment yields a satisfactory qualitative agreement in some cases,[8,59,80] whilst in others[51–55] it does not. The physical clarity of the theories of Manevich and co-workers[81–83] is so attractive that it has stimulated the desire to account (at least formally) for the causes of the disagreement between experiment and theory in the latter cases. If it is assumed that the increase in viscosity for BPS of the rubber–OAE type is indeed induced by large-scale concentration fluctuations, then in the most general case the above discrepancy may be caused by the molecular polydispersity of the polymer, which leads to the "smearing" of the limits of the thermodynamic stability of the BPS in the vicinity of which these fluctuations are in fact generated. Since this approach may prove useful in the analysis of the dynamic properties of any polydisperse systems,¶ we shall deal in greater detail with certain causes of the discrepancies between theory and experiment. The following fact may be regarded as established:

1. A polydisperse polymer is in fact a solution of fractions with different MW. It has been demonstrated[8,11,89–92] that, under certain conditions (the role of the MWD is of primary importance), there is even a possibility of microphase separation in mixtures of polymeric homologues.

2. The dissolution of a mixture of polymeric homologues in an organic solvent should lead to the establishment of equilibrium between the solutions of fractions with different MW.[13] One of the technological procedures for the fractionation of polymers is based on this precise factor. There is a possibility of at least two thermodynamically non-equivalent cases: (a) the solvent forms a molecular solution with all the fractions of the polymer; (b) for a specified composition and temperature, certain fractions of the polymer are insoluble.

3. Theoretical calculations[93] have shown that, when the blended polymers have similar MWD, then the CT for the blend is independent of composition; otherwise the CT shifts to the region of extreme compositions. Bearing in mind the previous conclusion, one may conclude that in a blend of two polydisperse polymers there is a range of CT determined by the CT of different fractions. The claim that there exists a region of consolute concentrations whose width should depend on the width of the MWD of the components is also valid.

¶ We may recall the anomalies in the viscoelastic properties of a series of other BPS have also been attributed[59] to the polydispersity of the components.

4. It follows from the study of Vinogradov and Malkin[1] that, in a flow of polydisperse polymers, the low-molecular-weight fractions can be regarded as plasticisers of the high-molecular-weight fractions. The converse claim that the high-molecular-weight fractions thicken the low-molecular-weight fractions should also be valid.

5. A decrease in the proportion of low-molecular-weight fractions in a polydisperse polymer should lead to an increase in the viscosity of the mixture.[1]

6. Allowance for the polydispersity of the components in the theory of the viscosity of BPS near the thermodynamic stability limit[82] leads to the conclusion that only some of the total number of molecules in the system participate in the generation of large-scale fluctuations. Consequently, only some of the molecules ensure the increase in the viscosity of the system. The laws governing the translational movement of the remaining BPS molecules determine their "entry" into a particular region of the phase diagram.

When applied to blends of a polydisperse rubber with OEA, the postulates formulated above mean that structural inhomogeneities should exist in such systems. The inhomogeneities are characterised by different local concentrations of the oligomer corresponding to the limits of its solubility in fractions with different MW: the low-molecular-weight fractions contain a relatively larger amount of the dissolved oligomer than the high-molecular-weight fractions; furthermore, the CT of the solutions of the low-molecular-weight fractions are lower than those of the high-molecular-weight fractions.

Overall, this implies that, when the polymeric component of the BPS has a fairly wide MW distribution, then the system always contains molecules "belonging" to different parts of the phase diagram. Consequently even insignificant changes in the MWD, the composition, or the temperature should entail a shift of the thermodynamic equilibrium established between solutions of different fractions and a redistribution of the molecules between different regions. This should inevitably lead to a change in the macroscopic viscosity of the system, which is made up of the viscosity of the regular solution and the corresponding corrections for the increase in viscosity due to the molecules "present" in regions II and IV (Fig.6). Furthermore yet another factor becomes significant: after the introduction of the oligomer, the molecules of the low-molecular-weight fractions of the polymer, which serve as plasticisers of the high-molecular-weight fractions in the absence of the solvent, cease to exert a plasticising effect and are therefore forced to enter a metastable or critical state participating in the generation of the large-scale fluctuations. The experimental "resultant" viscosity is in fact determined by the competition between all these factors.†

Thus the macroscopic viscosity of the mixture of a polydisperse polymer and the solvent can be represented as follows:

$$\eta_m = \eta_r + \Delta\eta_{cr}\varphi_{cr} + \Delta\eta_{sp}\varphi_{sp} + \Delta\eta_a\varphi_a - \Delta\eta_p\varphi_p, \qquad (12)$$

where η_r is the viscosity of the regular solution, $\Delta\eta_{cr}$ the positive "critical" correction taking into account the increase in the viscosity of the fraction of macromolecules (η_{cr}) in the critical region, $\Delta\eta_{sp}$ the positive (spinodal) correction determined by the appearance of large-scale fluctuations among the fraction of the macromolecules (φ_{sp}) near the spinodal curve, $\Delta\eta_a$ a positive correction (for "anti-plasticisation") determined by the fact that a proportion (φ_a) of the molecules of the low-molecular-weight fractions cease to plasticise the system, $\Delta\eta_p$ the correction (the "plasticising" correction) determined by the plasticising effect of the solvent and a proportion (φ_p) of the polymer molecules.

Evidently, $\Delta\eta_{cr}$, $\Delta\eta_{sp}$, and $\Delta\eta_a$ lead to an increase in the viscosity of the blend, while $\Delta\eta_p$ leads to its decrease. On this basis, a structural organisation of solutions of the individual fractions of the "polydisperse system" such that, according to Eqn.(12), the positive viscosity corrections predominate is presumably established under the experimental conditions selected[51-55] at low OAE concentrations. Other conditions being equal, an increase in the oligomer content increases φ_p and hence $\Delta\eta_p\varphi_p$ and therefore entails a decrease in η_m. After an increase in viscosity, its decrease is therefore observed on the "viscosity–composition" curve.

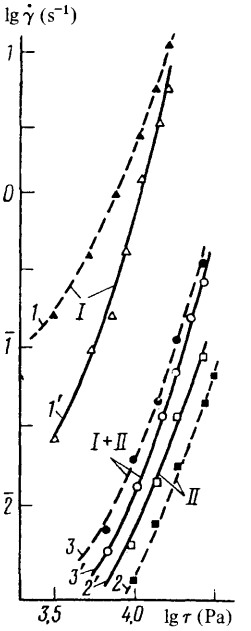


Figure 7. Flow curves for *cis*-polyisoprenes with MW = 5×10^4 (curves 1 and 1′) and 6.2×10^5 (curves 2 and 2′) and for their equimolar blend (curves 3 and 3′): 1)–3) without TGM-3; 1′)–3′) with 0.1 wt.% of TGM-3.[54]

† The contribution of the negative "osmotic" correction to the viscosity proposed by Mitlin and Manevich[83] is not taken into account below, because its quantitative relation with the "plasticising" viscosity correction ($\Delta\eta_p$) is not clear. It is suggested that the latter includes the "osmotic" correction.

The above schematic considerations make it possible to explain also why the position of the maximum on the experimental "viscosity–composition" curve is inconsistent with the theoretical prediction.[81-83] The cause of the discrepancy is the "diffuseness" of

the phase states of the individual fractions of the solutions of polydisperse BPS. This hypothesis has so far been confirmed only by indirect experiments.[54]

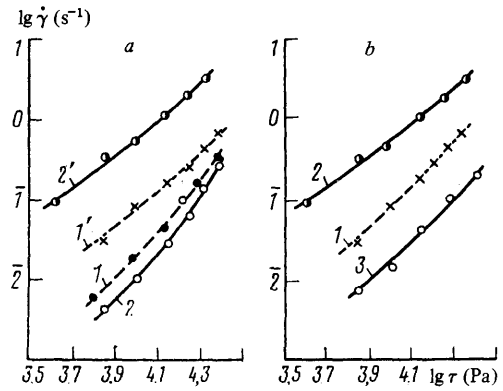


Figure 8. Flow curves for blends of *cis*-polyisoprenes with MW = 5×10^4 and 6.2×10^5: (a): 1) and 2) 1:1 concentration ratio; 1′) and 2′) 2:1 concentration ratio; 1) and 1′) without TGM-3; 2) and 2′) with 0.05 wt.% of TGM-3; (b): 1) without TGM-3; 2) with 0.05 wt.% of TGM-3; 3) with 0.05 wt.% of TGM-3; 2:1 concentration ratio.

It follows from Fig.7 that the increase in viscosity in the raw rubber–OAE system based on a high-molecular-weight raw rubber is manifested only when the system is "diluted" by the low-molecular-weight fraction of the same rubber. Since the relative increase in the viscosity is a maximum for BPS based on low-molecular-weight raw rubbers (Fig.3), it was to be expected that, in complex systems consisting of OAE and a blend of high- and low-molecular-weight raw rubbers, an increase in proportion of the low-molecular-weight fraction of the rubber component in the latter should increase the relative AIV. However, it follows from Fig.8 that, for the same OAE concentration, an increase in the proportion of the low-molecular-weight fraction in the raw rubber (the ratio of the low- and high-molecular-weight fractions is 2:1) not only does not intensify the effect but actually leads to a monotonic decrease in viscosity. This unexpected result is reasonable, provided that the hypothesis discussed above is valid. Indeed, the low-molecular-weight fraction is "responsible" not only for $\Delta\eta_{cr}$ and $\Delta\eta_{sp}$ but also for $\Delta\eta_p$. In the given instance, an increase in its concentration entails an increase in φ_p and an increase in the contribution to η_m by the negative viscosity correction. This results in a decrease in the experimental value.

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The anomalous dependence of the viscosity-dependent properties of BPS on concentration and temperature is a consequence of the characteristic features of their structural organisation for different parameters of state (in different regions of the phase diagram).

Although the true mechanism of the anomalous viscosity effect is still far from being understood, the studies in recent years have provided a physical foundation (the relation between the viscosity and the structural parameters of the BPS determined from its phase organisation) for the correct formulation of experimental and theoretical investigations of this phenomenon and have also extended the possibilities for its practical application.

The decrease in the viscosity of BPS (regardless of whether it is manifested in a traditional or anomalous manner) has a favourable effect on the processing of polymers and there are no fundamental problems as regards its practical use. The situation is much more complex with the practical application of the AIV. This is a many-sided problem. On the one hand, in many instances it is essential to increase the viscosity of compositions, for example, of paint and varnish systems, deposited on vertical and inclined surfaces. A fairly wide range of viscosities is inherent in the requirements which must be met by adhesive compositions, hermetic seals, etc. The regulation of viscosity (including its increase) is therefore an important technological procedure for the preparation of polymeric materials with specified properties. Another aspect of this problem consists in the fact that the understanding of the mechanisms of the increase in viscosity permits its prevention in those cases where it is undesirable.

As mentioned above, in BPS based on industrial polymers, which means polydisperse polymers, there are always microregions with a locally increased viscosity regardless of the macroscopic viscosity of the system as a whole. This property of BPS has made it possible to discover yet another application of the AIV phenomenon.[94] By increasing the viscosity in individual mixing stages, it has become possible to improve the dispersion of the filler in raw rubbers. The use of solvents with different solvent powers (the corresponding compositions with OEA) has made it possible to diminish simultaneously the energy expenditure on the processing.

The search for new practical applications of the increased viscosity effect is undoubtedly an interesting task in polymer materials science, but it can be solved successfully only if the true mechanisms of the rheological anomalies in binary polymer systems are clearly understood.

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Kinetics and Mechanism of the Inhibited Polymerisation of Vinyl Monomers

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New data on the kinetics and mechanism of reactions involving the inhibition of the radical polymerisation of vinyl monomers obtained during the last 10-15 years are described systematically and discussed. Equations describing the kinetics of the inhibited polymerisation, accompanied by side and secondary reactions such as additional initiation, chain regeneration, secondary inhibition, and inhibitor regeneration reactions are examined and analysed. The principal kinetic features associated with the structure of the monomer and the inhibitor, the type of initiation, and the influence of the medium are noted. Data are presented on the inhibiting activities of the compounds considered and the advantages of the latter relative to known stabilisers are demonstrated.
The bibliography includes 127 references.

CONTENTS

I. Introduction 1083
II. Equations for the inhibition reaction rate constant 1083
III. Inhibitors and mechanisms of the inhibition reactions under the conditions of radical polymerisation 1086
IV. Polymer stabilisers—effective inhibitors of radical polymerisation 1089
V. Characteristic features of the inhibition of bulk and heterophase polymerisation 1094

I. INTRODUCTION

One of the main criteria of a radical-chain polymerisation mechanism is the presence of inhibitors—substances whose addition in insignificant amounts to the reaction system can lower the rate of the process until its complete arrest.[1] The fundamental importance of inhibitors consists in the fact that they can be used as a kind of probe for the investigation of the polymerisation mechanism and as counters of active centres.

The practical value of inhibitors is determined by their application for the prevention of the undesirable formation of high-molecular-weight products under the conditions of the synthesis, purification, and storage of monomers.

The commonest inhibitors of the radical polymerisation of vinyl monomers are oxygen, quinones, phenols, aromatic amines, nitro-compounds, transition metal salts, and certain systems manifesting an increase in the reactivity of chemical compounds when they are mixed (synergism). In each specific case, the inhibiting activity of compounds of the above classes is different and depends significantly on particular physicochemical factors.

The retardation of polymerisation is associated with the interaction of active radicals with a relatively ineffective (weak) inhibitor, which results either in a decrease in the concentration of the active centres or in the formation of species incapable of propagating the kinetic and molecular chains.

In the presence of highly effective (powerful) inhibitors, the reaction is accompanied by an induction period during which there is no polymerisation. At the end of the induction period, steady-state kinetics are usually established and the rate of the process can be identical with the rate of the inhibited polymerisation or can be lower than the latter. The character of the dependence of the induction period τ on the intial inhibitor concentration $[X]_0$ is determined by the structures of the inhibitor and the monomer, the method and mechanism of initiation (thermal, material, etc), the nature of the initiator (azo-compound, peroxide, etc) and certain other physicochemical conditions in polymerisation.[2-6] A linear dependence of the induction period in polymerisation on the inhibitor concentration is usually encountered. In many cases, the induction periods increase faster or more slowly with increasing inhibitor concentration, which is usually due to the regeneration of the inhibitor or the additional initiation (or regeneration) of the chain.[6] During these reactions, the relation between the kinetic parameters and the concentrations of the reaction system components is various.

For different mechanisms of the interaction of the inhibitor with the active radicals, the stoichiometric inhibition coefficient μ may lie within a fairly wide range.

II. EQUATIONS FOR THE INHIBITION REACTION RATE CONSTANT

1. The Bagdasar'yan–Bamford Equation

The time variation of the rate of inhibited polymerisation makes it possible to find the inhibition reaction rate constant.[3,6] The mechanism of the radical-chain polymerisation in the presence of a highly effective inhibitor may be formulated in the following simplest form:

$$\begin{aligned} I &\xrightarrow{K_{cons}} 2R_0, \\ R_0 + M &\xrightarrow{K_i} R, \\ R + M &\xrightarrow{K_p} R, \\ R + R &\xrightarrow{K_t} \text{polymer}, \\ R + X &\xrightarrow{K_X} \text{polymer}, \end{aligned}$$

where I, M, and X are the initiator, monomer, and inhibitor molecules, R_0 and R are the primary and polymeric radicals, and K_{cons}, K_i, K_p, K_t, K_x are the rate constants for the corresponding elementary reactions.

Using the steady-state relations for any instant during the induction period,

$$W_i = K_t[R]^2 + K_x[R][X], \quad (1)$$

(W_i is the rate of initiation), and for the rate of consumption of the inhibitor,

$$-\frac{d[X]}{dt} = K_x[R][X], \quad (2)$$

it is possible to obtain the Bagdasar'yan–Bamford equation:

$$F_1 \equiv -\frac{1}{\varphi} + \ln\frac{1+\varphi}{1-\varphi} = \frac{K_x W_{max}}{K_p[M]}t + A, \quad (3)$$

in which the reduced rate φ is equal to the ratio of the rate of reaction at any instant to the steady state rate of polymerisation W/W_{max} and A is the constant of integration.

Eqn.(3) describes the polymerisation kinetics in the presence of an "ideal" inhibitor.[2,7] The Bagdasar'yan–Bamford equation is applicable only to inhibited polymerisation in which side reactions take place without the participation of the inhibitor itself and their contribution to the overall process kinetics does not vary with time. It is also valid in the presence of a chain regeneration reaction. In all these cases, the dependence of the duration of the induction period in the polymerisation reaction on the initial inhibitor concentration is usually linear.

The fundamental importance of Eqn.(3) is determined by two factors. Firstly, the plot of the function against time is linear and the inhibition constant can be found from its slope.[6] Secondly, the relation

$$W_i = \frac{\mu[X]_0}{\tau}, \quad (4)$$

which is the theoretical basis of the universal inhibition methods for the rigorous determination of the rate of initiation, can be obtained from it.

2. The Equation Describing the Kinetics of Inhibited Polymerisation Taking into Account Chain Initiation by the Inhibitor Molecules

The time variation of the rate of polymerisation can be influenced by the reaction involving the additional initiation by inhibitor molecules, which is characteristic of certain substances of both radical and non-radical nature. In such cases, special relations must be used to find the inhibition constants.[8,9]

In the interaction of the inhibitor with the monomer, leading to the formation of active centres, the steady-state relation (1) changes:

$$W_i + K_i[X][M] = K_x[R][X] + K_t[R^2], \quad (5)$$

(K_i is the rate constant for the additional initiation reaction) and the consumption of the inhibitor obeys the equation

$$-\frac{d[X]}{dt} = K_i[X][M] + K_x[R][X]. \quad (6)$$

At the end of the induction period, the reaction takes place at a steady-state rate W_∞ and

$$W_i = K_t[R]_\infty^2. \quad (7)$$

Ultimately, the kinetics of the inhibited polymerisation are described in this instance by the equation

$$F_2 \equiv -2\theta\ln(\varphi+\theta) - (1-\theta)\ln(1-\varphi) + (1+\theta)\ln(1+\varphi) + \frac{1/\theta-\theta}{2}\ln\left|\frac{\varphi-\theta}{\varphi+\theta}\right| = \frac{K_x W_\infty}{K_p[M]}(1-\theta^2)t + B, \quad (8)$$

from which it is possible to find the inhibition constant K_x/K_p, provided that the parameter $\theta = K_i[M]/K_x[R]_\infty$ is known. The quantity θ can be found in its turn from the reduced rate φ at the point of inflection (φ_b) in the S-shaped relation between the rate of inhibited polymerisation and time. If φ obeys Eqn.(8), then it follows from the condition for the point of inflection that

$$\theta^3 + \frac{2\varphi_b}{1+\varphi_b^2}\theta^2 - \frac{2\varphi_b^4-\varphi_b^2}{1+\varphi_b^2}\theta + \frac{\varphi_b^5+2\varphi_b^3-\varphi_b}{1+\varphi_b^2} = 0. \quad (9)$$

If the kinetics of the inhibited polymerisation are described by the Bagdasar'yan–Bamford equation, then $\theta_b = 0.643$. In the presence of additional initiation, φ_b varies from 0.643 to 1.0. Fig.1 illustrates the dependence of θ on φ_b calculated by Eqn.(9).

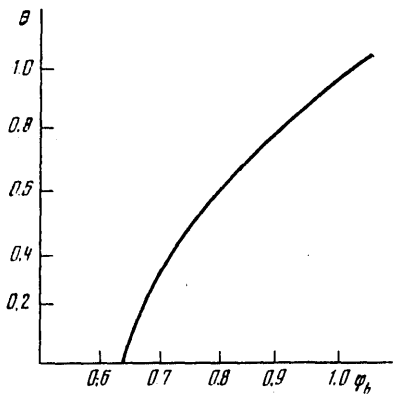


Figure 1. Dependence of the parameter θ on φ_b according to Eqn.(9).[9]

Eqn.(8) can be transformed into

$$F_2 \equiv K_i[M]\left(\frac{1}{\theta}-\theta\right)t + B,$$

which makes it possible to find the additional initiation rate constant K_i.

3. Kinetic Equation Taking into Account the Effects of the Secondary Inhibition (Retardation) of Polymerisation

The effect of a highly efficient inhibitor on polymerisation can produce not only an induction period but can also lower the rate of reaction with increasing inhibitor concentration.[6,10] The decrease in the concentration of growing chains is usually associated with their interaction with the primary inhibition products Y:

$$R + X \xrightarrow{K_X} Y;$$
$$R + Y \xrightarrow{K_Y} \text{polymer}.$$

In a steady-state process, we have during the induction period

$$W_i = K_X[R][X] + K_Y[R][Y] + K_t[R]^2.$$

The consumption of the inhibitor is described by Eqn.(2) in this case also. When account is taken of the material balance relation $[Y] = [X]_0-[X]$ and the steady-state equations for the non-inhibited polymerisation

$$W_i = K_t[R]^2 \tag{10}$$

and at the end of the induction period

$$W_i = K_t[R]_\infty^2 + \alpha K_Y[R]_\infty[X]_0 \tag{11}$$

(α is the stoichiometric secondary inhibition coefficient), we obtain

$$F_3 \equiv -\frac{1}{\varphi} - \ln(1-\varphi) + (1-\varphi_\infty^2)\ln\varphi + \varphi_\infty^2 \ln\left(\varphi + \frac{1}{\varphi_\infty^2}\right) = \frac{K_X W_\infty}{K_p[M]} t + C. \tag{12}$$

In the last equation, φ is the ratio of the rate of polymerisation at any instant W_t to the steady-state rate of the inhibited reaction W_∞ and φ_∞ is the ratio of W_∞ to the steady-state rate of the non-inhibited process W.

Thus the primary inhibition constant K_X/K_p is determined from the slope of the linear time variation of F_3. Evidently, if the inhibition products Y do not have a retarding influence on the subsequent polymerisation ($W\infty = W$ and $F_\infty = 1$), then Eqn. (12) becomes identical with Eqn.(3).

The secondary inhibition (retardation) rate constant K_Y is calculated from the relation obtained from a calculation for the polymerisation scheme in the presence of a relatively ineffective inhibitor[3,6] and the analysis of the non-steady state equation (11):

$$K_Y = \frac{(1-\varphi^2)K_t W}{\alpha\varphi K_p[M][X]_0}$$

4. Refinement of the Conditions Governing the Applicability of the Kice Equation to the Solution of the Converse Kinetic Problem in Inhibited Polymerisation

Studies have been published comparatively recently[11-13] in which, on the one hand, a new approach was described to the analysis of the Kice equation[14] and, on the other, the conditions governing its application were defined more rigorously.

Kice's fundamental assumptions concerned two factors: the inhibitor does not participate in the chain initiation stage and the quadratic chain termination rate constant is independent of the presence of the inhibitor.

Smirnov and Karapetyan[11] suggested that only one evident simplifying condition be used—the quasi-steady-state nature of the active and inactive radicals. As before, in this instance the reduced rate φ is determined by the ratio of the concentrations of the growing chains in the presence and absence of the inhibitor, namely $[R]_X$ and [R] respectively:

$$\varphi = \frac{W_X}{[M]_X} \Big/ \frac{W}{[M]} = [R]_X/[R].$$

The usual mechanism of radical polymerisation in the presence of a molecular inhibitor was supplemented by reactions involving initiation by the inhibitor

$$R_0 + X \xrightarrow{K_{iX}} R_X,$$

chain regeneration

$$R_X + M \xrightarrow{K_r} R$$

and chain cross-termination

$$R + R_X \xrightarrow{K_{tX}} \text{inactive product}.$$

(K_{iX}, K_r, and K_{tX} are the rate constants for the corresponding reactions).

If $\varphi^2/(1-\varphi^2) \gg K_rK_t/K_pK_{tX}$, which is always valid for typical inhibitors ($K_r/K_p \gg 1$, $\varphi \gg 0.1$), then the kinetics of the inhibited polymerisation are described by the equation

$$A\left(\varkappa + \frac{2\epsilon}{\varphi}\right) = C + B, \tag{13}$$

where

$$\varkappa = K_X[X]/\{K_{cons}f[I](K_t)_{X=0}\}^{0.5},$$
$$C = K_rK_tK_X[M][X]/K_{tX}\varkappa,$$
$$\epsilon = K_{iX}[X]/(K_{iX}[X] + K_{iM}[M]).$$

(K_{iM} is the rate constant for the reaction $R_0 + M \rightarrow R$).

$$A = \frac{\theta}{2}\left(\frac{B}{\varphi} - 1\right),$$
$$B = \varphi\left(1 + \theta\frac{1-\gamma\varphi^2}{\varphi^2}\right)^{0.5},$$
$$\gamma = (K_t)_X/(K_t)_{X=0},$$
$$\theta = 4(K_t)_{X=0}K_{tXX}/K_{iX}^2.$$

(K_{tXX} is the rate constant for the reaction $R_X + R_X \rightarrow$).

When $\epsilon = 0$ and $\gamma = 1$, Eqn.(13) becomes identical with the Kice equation:

$$A\varkappa = C + B.$$

in which A and B depend only on φ and θ. Under the usual inhibition conditions, the reduced rate φ is a function of κ, C, and θ. The deviations from the kinetics described by Eqn.(13) are observed for low values of φ and unduly high rates of chain regeneration.

The relation $\theta \ll 1$ holds for the inhibited polymerisation. Here $B < 1$ for any φ and the chain regeneration parameter C can assume any values, including $C \gg B$. When the latter inequality holds, the reduced rate and the expressions for the rates of inhibited polymerisation are determined by the mechanism of the inhibition reaction.

When the active radical R interacts with the inhibition product, we have

$$\varphi = (C/\varkappa)^{0.5}$$
$$W_X = K_p (K_{cons} f K_r / K_X K_{tX})^{0.5} [M]^{1.5} [I]^{0.5} [X]^{-0.5}.$$

If chain termination takes place via the interaction of inhibitor radicals with one another, then

$$\varphi = 2C/\varkappa\theta^{0.5},$$
$$W_X = \{K_p K_r (K_{cons} f / K_{tXX})^{0.5} / K_X\} [M]^2 [I]^{0.5} [X]^{-1}.$$

Both expressions for the rate of the inhibited polymerisation show that the very fact of inhibition does not in any way imply an increase in the kinetic order with respect to the initiator.

In the presence of stable radicals and transition metal ions not involved in the initiation of the reaction and not promoting the chain regeneration, the inhibition mechanism changes. The inhibition steps are expressed in the form

$$R + X \xrightarrow{K_X} \text{inactive products},$$
$$R + M^{2+}L_2^- \xrightarrow{K_X} M^{3+}L_2^-R^-,$$
$$R + M^{3+}L_3^- \xrightarrow{K_X} M^{2+}L_2^- + RL\,(L = \text{ligand}).$$

In such cases the inhibition reaction rate constant can be found from the equation

$$K_X = \frac{2(1-\varphi^2)(K_{cons} f [I] K_t)^{0.5}}{\varphi [X]}$$

This equation is identical with the relation presented previously and obtained for the rate constant for the interaction of the inhibitor with the polymeric radical K_Y under weak inhibition conditions where there are no induction periods and only a decrease in the rate of polymerisation is observed. However, stable radicals and transition metal salts are usually effective inhibitors of radical polymerisation. In their presence, the rate of polymerisation and hence also φ vary with time and are virtually zero during the induction period, which reduces significantly the possibility of employing the last equation for finding the rate constant for relatively ineffective inhibition.

III. INHIBITORS AND MECHANISMS OF THE INHIBITION REACTIONS UNDER THE CONDITIONS OF RADICAL POLYMERISATION

Fairly extensive experience has now accumulated concerning, on the one hand, the search for effective stabilisers of vinyl monomers and, on the other hand, the determination of the kinetic features and mechanisms of the inhibiting action of different classes of substances. In general, one should note that the problem of the chemistry of the inhibition of radical polymerisation had not received due attention for a long time. At the same time, these questions are always of current interest, especially in connection with the selectivity of the action of inhibitors. Depending on the reactivity of the monomer (or its polymeric radical), temperature, the presence of various kinds of admixtures in the medium, the structure of the inhibitor itself, etc., the mechanism of the interaction of the inhibitor with the active radical can in many instances be ambiguous.

The first more or less systematic data concerning these questions have been published in monographs.[2-5] Subsequently, in the course of one and a half decades, only isolated studies appeared in the scientific literature. The most interesting of the latest reviews in which a wide range of inhibitors and the mcehanisms of their action are considered are those of Lazareva and Sidorov[15] and Barabashina et al.[16] The principal value of these reviews consists in the fact that they deal not only with the methods for the stabilisation of pure monomers but attention has been given to information about the most probable mechanisms of the inhibition of polymerisation occurring in individual stages of the synthesis of the monomers and for different ways of isolating, purifying, fractionating, and processing such monomers.

A chapter in the monograph of Gladyshev and Popov is devoted to questions of the regulation of the gel-effect in radical polymerisation with the aid of relatively ineffective inhibitors.[17]

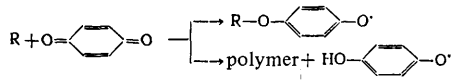
Apart from the previously known classes of stabilisers enumerated above, many inhibitors and inhibiting systems have been described in the patent literature. For example divinylacetylene,[18] hexamethylenetetramine,[19] salts of dibutyldithiocarbamic acid,[20] the composition containing phosphoric acids and (or) phosphoryl oxide, cresol, benzaldehyde,[21] aromatic amines with different structures,[22-27] *p*-methoxyphenol[28] and other phenols,[29] combinations of inhibitors of the amine and phenolic types,[30] compounds containing the nitroso-group linked to a carbon atom of the aromatic ring,[31] etc., have been proposed for the inhibition of the polymerisation of acrylates and methacrylates.

There have been comparatively few studies devoted to the relation between the structure of polycondensed aromatic hydrocarbons and their ability to inhibit the polymerisation of vinyl monomers. These questions were raised for the first time and in several studies.[32-35] It has been shown[36] that condensed aromatic hydrocarbons do not influence the chemically initiated polymerisation of methyl methacrylate but do inhibit the photosensitised reaction, reducing its rate without inducing an induction period. The inhibiting activity increases in the sequence naphthalene < phenanthrene < anthracene < chrysene. The inhibiting effect of the above substances is associated with their transition to the triplet state under the influence of light.

In their study of the polymerisation of vinyl acetate initiated by azobisisobutyronitrile in the presence of aniline and its derivatives,[37] Simonyi and Tudos[37] suggested that, when the substituent is changed, the stoichiometry of the inhibition reaction does not change but a decrease in the inhibition rate constant has been observed. Thus the constants K_X for aniline, *N*-methylaniline, and *NN'*-dimethylaniline are respectively 17, 6, and 0.7. After the introduction of a substituent into the benzene ring in the *para*- and *meta*-positions, the activity of the inhibitor is described by the Hammett equation. *ortho*- and poly-substituted anilines exhibit a reduced reactivity.

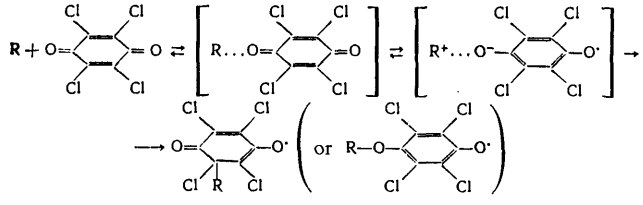
Many quinonoid compounds and their derivatives effectively inhibit radical polymerisation. The inhibiting activity of quinones is determined not only by their chemical structure and oxidation-reduction potential but also by the electron-donating capacity of the

macroradical and the polarity of the medium (usually the monomer itself).[38] Depending on these factors and the physicochemical conditions in the reaction, there is a possibility of recombination and disproportionation:[3]



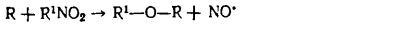
or the formation of an inactive radical via an intermediate charge-transfer complex (CTC).[39,40]

Further studies showed[41] that the rate-limiting stage in the interaction of the active radical with quinones is the conversion of the CTC into the inhibitor radical. The reaction involving methacrylates and acrylates is slow but can be accelerated by the addition of certain electron-donating compounds, for example, phenothiazine. The mechanism of the inhibition by quinones has been represented as follows in the case of the polymerisation of methyl methacrylate in the presence of chloranil:

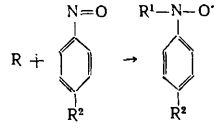


Regardless of the mechanism of the interaction of the quinone with the growing radical, the stoichiometric inhibition coefficient is in all cases close to two.

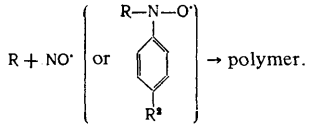
Polymerisation in the presence of nitro- and nitroso-derivatives is usually accompanied by an induction period and retardation of the reaction.[16] Compared with quinones, nitro-compounds reduce the rate of the process to a lesser extent, since their interaction with macroradicals is more difficult. Their inhibiting capacity is determined by the nature of the monomer, the type of polymerisation (in bulk or in solution), increasing with increase in the number of nitro-groups. From the mechanism of the inhibition of polymerisation by substances in this class,[16,42-45] it also follows that $\mu \simeq 2$:



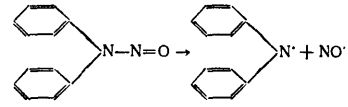
or



and further



Nitro-compounds can interact with growing chains but also with primary initiator radicals.[46] In certain cases, the nitroso-compound can decompose with formation of nitric oxide and a product having the properties of a stable radical:[47]



The stoichiometric inhibition coefficients of dimethyl-*p*-nitrosoaniline and *p*-nitrosodiphenylamine in the polymerisation of styrene, acrylonitrile, and methyl acrylate depend on the monomer concentration.[48] For example, the decrease in the mole fraction of the monomer from 1 to 0.3 in the acrylonitrile–DMF–*p*-nitrosodiphenylamine system entails an increse in μ from 0.86 to 1.8, while in the methyl acrylate–DMF–*p*-nitrosodiphenylamine system μ increases from 1.54 to 1.94 as the mole fraction of the monomer is reduced from 1 to 0.5. Tudos and co-workers[48] explained the changes in the stoichiometric coefficient on the basis of the hot radical theory.[48]

The results of studies on the inhibiting capacity of nitroso-compounds under radical polymerisation conditions proved to be closely related to the problem of the removal of the stabiliser from the monomer before its conversion into the polymer. This is usually achieved by fractionation with preliminary extraction of the inhibitor. The optimum solution of this problem is achieved by the monomer stabilisation method in which the inhibitor is effective during the storage of the monomer but does not affect its polymerisation.

One of the versions of the solution of this problem consists in the use of inhibitors interacting with the components of the reaction medium (for example, with the initiator) and then losing their activity. The radical-anion complexes of tetracyanoquinodimethane may serve as an example of inhibitors of this kind.[49,50]

Another version involves the use of inhibitors which are sparingly soluble in the monomers. During the storage of the latter, when the rate of the initiation of the polymerisation is low, there is sufficient dissolved inhibitor for effective stabilisation. However, this concentration of the inhibitor does not have a significant influence on the polymerisation under the properties of the high-molecular-weight products formed. The results obtained in the study of polymerisation in the presence of added cupferronates (ammonium salts of *N*-nitroso-*N*-phenylhydroxylamine and its derivatives) in fact correspond to this particular version.[51] Sodium, potassium, ammonium, and copper cupferronates inhibit effectively the polymerisation of acrylates and methacrylates in solution in DMF. The duration of the induction period increases linearly with increasing concentration of the additives. In contrast to the polymerisation of styrene, for which the stoichiometric inhibition coefficient is two[16] (analogously to the mechanism adopted for inhibition by nitro- and nitroso-compounds), in the polymerisation of acrylates and methacrylates, μ = 1.5. In these cases, an interaction has been observed between the cupferronates and the monomers with formation of free radicals and a decrease in μ.

In the polymerisation of methyl acrylate, butyl acrylate, and methyl methacrylate, the dependence of the induction period on the concentrations of the cupferronates is non-linear and the steady-state rate of the inhibited reaction is less than that of the non-inhibited reaction.

One of the features of the above salts of practical importance is that they inhibit polymerisation not only in air but also under oxygen-free conditions.

The differences in the influence of various cupferronates on polymerisation are caused by their different solubilities. Copper and sodium cupferronates exhibit the highest and lowest solubilities respectively in acrylic monomers. The results of Gol'dfein et al.[51] make it possible to plot calibration relations for the polymerisation inhibition periods observed in saturated solutions of cupferronates in monomers as a function of the concentration of the salts.

The interaction of cupferronates with acrylates and methacrylates leads to their deactivation and is one of the causes of the non-linearity of the concentration variation of the induction period. After a time, the cupferonates gradually decompose. In terms of stability, they can be arranged in the following sequence: copper > sodium > potassium > ammonium cupferronates. Furthermore, the degree of their deactivation depends on the chemical structure of the monomer: it is highest in methyl methacrylate and lowest in methyl acrylate.

At certain stages in the synthesis of the monomers, the reaction mixtures contain fairly large amounts of water. The presence of water in the monomers influences also the solubility of the cupferronates and hence their inhibiting activity. The presence of water in the monomer has a greater effect on the induction period in polymerisation the higher the solubilities of the cupferronate and water in the monomer.

Metal salts have different effects on the kinetics and mechanism of the radical polymerisation of vinyl monomers.[2-4] Thus a concentration-dependent inversion of the catalytic properties is characteristic of iron and copper chlorides.[52,53] The inhibiting effect of aliphatic acid salts depends on the nature of the metal in the salt and also on the medium in which the reaction takes place (in bulk or in solution) and on the size of the anion.[54] The inhibiting influence of zinc, cobalt, and lead stearates on the polyerisation of styrene and methyl methacrylate, initiated by the inhibition in such cases consists in the interaction of the active radical with the intermediate complex formed between the stearate and the peroxide. Transition metal chlorides and aliphatic acid salts have not found extensive practical applications.

The influence of the medium on the kinetic parameters of the inhibition of the polymerisation of vinyl monomers in the presence of iron and copper chlorides has been analysed.[57] For example, in the inhibition of the polymerisation of acrylonitrile in aqueous sodium thiocyanate solution, the inhibition constant increases by 2–3 orders of magnitude compared with the polymerisation in solution in DMF.[58]

Metal salts of dialkyldithiocarbamic acid have come to be recommended as effective inhibitors of the polymerisation of acrylic monomers. These compounds readily accept peroxy- and alkyl radicals. The mechanism of the inhibiting effect is complicated in the presence of hydroperoxides, because the interaction of the salt with the active radical or hydroperoxide results in the formation of a paramagnetic compound with an enhanced inhibiting capacity.[59] The efficiency of the inhibition then depends on the ratio of the concentrations of the components of the reaction system and on the nature of the metal salts,[60] increasing in the sequence

$$Zn(S_2CNR_2) < Ni(S_2CNR_2)_2 \ll Cu(S_2CNR_2).$$

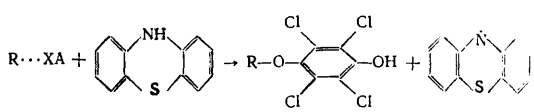
The mechanism of the inhibition of polymerisation by dialkyldithiocarbamates cannot be regarded as established at the present time. Some workers[61] believe that the site in the salt molecules most vulnerable to attack by active radicals is at the sulphur atoms. Others[62,63] postulate interaction with the metal ion and that this is responsible for the transfer of electrons from the ligand to the radical, which is feasible in view of the presence of a covalent bond between the metal and sulphur atoms.[64]

Copper diethyldithiocarbamate (CDTC) exhibits effective inhibiting activity in the polymerisation of acrylic acid in aqueous solution and in solutions in acetic acid and isopropyl acetate.[65] In all cases, the dependence of the induction period on the salt concentration is linear and the stoichiometric inhibition coefficients are greater than unity and depend on the type of solvent. The highest inhibiting capacity of CDTC has been observed in aqueous solution and the lowest in acetic acid. The values of μ obtained in the polymerisation of acrylic acid in air and under oxygen-free conditions are virtually identical, which indicates the same stoichiometry of the interaction of CDTC with alkyl and peroxy-radicals. The mechanism of the inhibition in these cases is apparently analogous to the mechanism of the inhibition of oxidation reactions by phosphorodithioates[66] accompanied by electron transfer to the active radical. The increase in μ (in excess of 2) can be associated with the interaction of the radicals with two sulphur atoms.

The rate of polymerisation of acrylic acid in organic media is fairly considerably reduced compared with the rate in aqueous solution. This is due to the formation of complexes by acetic acid and isopropyl acetate with the polymeric radicals[67,68] and the reduction of the reactivity of the latter. The interaction of these solvents with the growing chains is also responsible for the decrease in μ in the polymerisation of acrylic acid in solutions in acetic acid and isopropyl acetate compared with the reaction in water. The primary (K_X/K_p) and secondary (K_Y/K_p) inhibition constants have been found for the systems indicated by Eqns.(14) and (15) respectively.

A mixture of chloranil (CA) and phenothiazine (PT) proved to be an effective inhibiting system.[69] In contrast to the polymerisation of styrene, where chloranil is a powerful inhibitor,[70] in methyl acrylate only a slight inhibition is observed and CA has no influence on the polymerisation of methyl methacrylate. On the other hand, when PT or the oligomeric product of its oxidative condensation (OPT) was added, a synergistic effect with a distinct induction period was observed.[71,72] It has been shown[69] that the rate-limiting stage of the inhibition process involves the interaction of the growing chain with a CA molecule and not with the PT...CA complex. The sharp increase in K_X, approximately by two orders of magnitude in the presence of PT or OPT, can be satisfactorily accounted for by the mechanism above.[41]

The interaction of PT with CTC leads to the formation of the PT· radical:

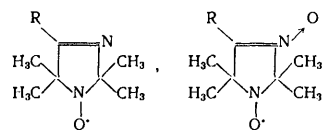


The PT· radical can interact with R, M, and XA to form a new radical capable of terminating yet another chain. However, the stoichiometric inhibition coefficient proved to be less than two which is due to the regeneration of the chain in the interaction of PT· with a methyl methacrylate molecule. In the polymerisation of methyl acrylate, the inhibiting effect of the CA–PT system is appreciably smaller. In this case not only the active radicals but also the CTC enter into the reaction with CA. Thus the structure of the monomers and the donor–acceptor properties of the monomers and the growing radicals play a decisive role in the inhibition mechanism.

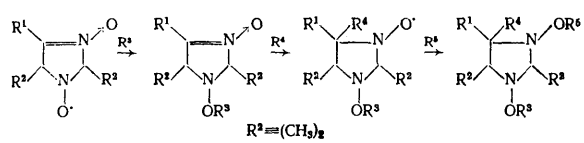
The study of the kinetics of the inhibition of the polymerisation of vinyl monomers in the presence of binary systems has been suggested.[73,74] It has been shown that mixtures of CA with triethylamine and also of anthracene with phenothiazine and oligophenothiazine effectively inhibit the radical polymerisation of methyl methacrylate. The existence of critical inhibitor and initiator concentrations is associated, according to the authors, with the inhibiting effect of *NN*-diethylaminovinyltrichloro-*p*-benzoquinone, formed as a result of the conversion of the CTC into a radical pair. The observed synergistic effect can be explained by the radical-chain reactions involving the consumption of the inhibitors.

Stable radicals incapable of recombining are effective inhibitors of the polymerisation of vinyl monomers. Data concerning the use of hydrazyl, verdazyl, iminoxy-, and arylnitroxy-radicals in addition to certain radical-anions as spin-trapping agents as well as polymerisation in the presence of these substances, indicating the complexity of the inhibition mechanism, have been quoted in a recently published review.[50]

Nitroxy-radicals of the type of imidazoline and imidazolidine proved to be extremely interesting from both theoretical and experimental standpoints.[75,76] They belong to the class of five-membered nitrogen-containing heterocyclic free radicals:



Compared with the types of stable radicals listed above, the nitroxy-radicals based on imidazoline and imidazolidine have a number of advantages. The additional nitrogen atom of the *N*-oxide group combined with the functional group in the 4-position in the heterocycle makes it possible to achieve complex formation and cyclometallation without the involvement of the radical centre. The presence of the imine or imine *N*-oxide (nitrone) group in the imidazoline molecule leads to a much greater stability of the nitroxy-radical in an acid medium, which is an important factor in the practical employment of such radicals as inhibitors of polymerisation, occurring, for example, under the conditions of the synthesis of methacrylates. Imidazoline *N*-oxides, as agents interrupting oxidation chains and as trapping agents for short-lived radicals of various types, should manifest the highest inhibiting activity under these conditions:



According to the scheme formulated above, the stoichiometric inhibition coefficient should be greater than unity.

It has been shown[77,78] that the 2,2,5,5-tetramethyl-3-oxo-4-phenylimidazolin-1-yloxy-radical (TMPIZ) effectively inhibits the polymerisation of styrene and methyl methacrylate. It was of interest that the form of the dependence of the duration of the induction period on the initial concentration of the stable (linear) radical and the stoichiometric inhibition coefficients (μ = 1.5 for styrene and μ = 1.25 for methyl methacrylate) are independent of the nature of the initiator (an azo-compound or a peroxide), as has been observed, for example, for iminoxy-radicals and especially for arylnitroxy-radicals.[50]

TMPIZ has a weak inhibiting effect on the polymerisation of methyl methacrylate in the presence of both concentrated and dilute sulphuric acid. At the same time, the form of the dependence of the steady-state rate on the TMPIZ concentration is determined by the concentration of sulphuric acid in water. The inhibition constants K_X/K_p are therefore found by taking into account the kinetics of the polymerisation at the end of the induction period—using Eqns.(3) and (12) respectively in the presence of concentrated and dilute acid.

The inhibiting activity of TMPIZ, a nitroxy-radical derived from imidazoline, in an acid medium made it possible to use it for the determination of the rate of initiation of the polymerisation by sulphuric acid and also of the rate constants for the chain propagation and termination reactions corresponding to different contents of the acid in water and in the reaction system.[78]

In the inhibition of the thermal polymerisation of methyl methacrylate in the presence of sulphuric acid, the dependence of the induction period on the TMPIZ concentration is markedly more non-linear than might have been expected in the presence of an additional initiation reaction. It is most likely that this is associated with the characteristics of the mechanism of the thermal initiation. Some workers[79,80] suggest that the thermal polymerisation is initiated by triplet radicals and that all the radicals interact with the inhibitor. Others draw attention to the possibility of the interaction of the inhibitor with the monomer[81-83] and of reactions between the inhibitor and an intermediate formed at a rate exceeding the rate of initiation.[84] The kinetics of the inhibited polymerisation have been analysed in greatest detail taking into account these reactions in relation to styrene,[85] where the inhibitors were divided by the author into two groups—interacting and not interacting with the intermediate, which is a biradical in thermal initiation.

IV. POLYMER STABILISERS—EFFECTIVE INHIBITORS OF RADICAL POLYMERISATION

1. Polymerisation in Bulk and Certain Features of the Inhibition of Thermo-oxidative Polymerisation

Despite the fundamental difference between their structures, aromatic amines and phenols are often combined in a single group of inhibitors.[86] In the presence of oxygen, these compounds inhibit effectively radical polymerisation, but in its absence they manifest only the properties of weak inhibitors.[17] Furthermore, both amines and phenols tend to form hydrogen bonds with peroxy-radicals, which tends to increase the rate of the inhibition reaction.

In many cases the abstraction of a hydrogen atom from the reagent by an active radical is the decisive elementary step in the initiation stage, for example:

$$RO_2 + R^1—NH—R^2 \rightarrow ROOH + R^1—\dot{N}—R^2,$$

$$R \text{ (or } RO_2) + R^1—\dot{N}—R^2 \rightarrow \text{polymer},$$

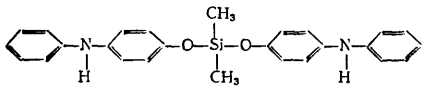
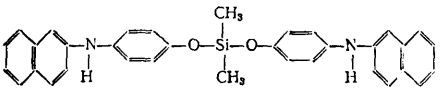
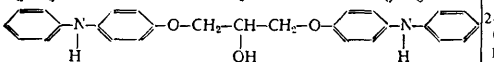
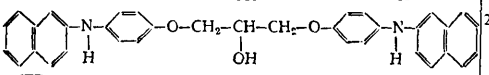
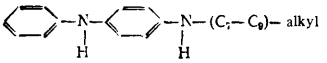
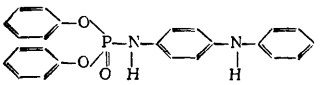
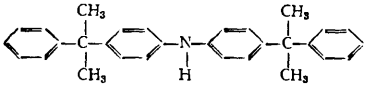
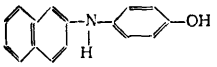
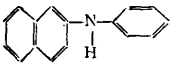
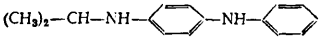
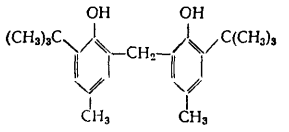
$$R^1—\dot{N}—R^2 + R^1—\dot{N}—R^2 \rightarrow \text{inactive product}.$$

The high rate of interaction of RO_2 with the amine molecule is then caused by the formation of polar activated complexes $ROO^-...H^+$

...N⁻< and not by the low energy of the N–H bond. The inhibiting activity of aromatic amines depends on the polarity of the substituents in the benzene ring: electropositive substituents increase and electronegative substituents diminish the inhibiting effect.

During the last decade, new highly effective inhibitors of the polymerisation of vinyl monomers in the presence of oxygen have been found in the class of aromatic amines,[87-94] which had been synthesised previously as additives to polymeric materials for their stabilisation. These compounds, some of which are listed in Table 1, are readily soluble in many organic solvents, acrylic and methacrylic monomers, and concentrated sulphuric acid.

Table 1. New effective inhibitors of the polymerisation of vinyl monomers.[87-94]

Structural formula	Chemical name	Technical name
	dimethyldi-(*p*-phenylamino-phenoxy)silane	S-1
	dimethyl(β-naphthylamino-*p*-phenoxy)silane	S-41
	2-hydroxy-1,3-di-(*p*-phenylamino-phenoxy)propane	S-47
	2-hydroxy-1,3-di-(β-naphthylamino-*p*-phenoxy)propane	S-49
	*N*-(C_7–C_9)-alkyl-*N'*-phenyl-*p*-phenylene diamine	S-789
	(*p*-phenylamino-phenyl) amide of diphenylphosphoric acid	S-875
	4,4'-bis(αα'-dimethyl benzyl)-diphenylamine	S-933
	*p*-hydroxyphenyl-β-naphthylamine (hydroxyneozone)	HN
	phenyl-β-naphthyl-amine	neozone D
	phenyl-*p*-isopropyl-amino phenyl-amine	diaphen FP
	2,2'-methylenebis-(6-t-butyl-4-methyl)phenol	22-46

In the presence of the above amines, the oxidative polymerisation of styrene and acrylic and methacrylic acids and their esters, initiated by azobisisobutyronitrile (ABIN), is preceded by induction periods whose duration increases linearly with increase in the concentration of the additive. As can be seen from Fig.2, if the induction period is adopted as the criterion of the inhibiting activity, all the substances presented are found to be superior to hydroquinone—the most widely used stabiliser at the present time. The width of the transitional region between the non-steady-state and steady-state kinetics depends little on the inhibitor structure. Under oxygen-free conditions, the test substances have almost no inhibiting influence on the polymerisation of acrylates and methacrylates in bulk for the initial degrees of conversion.

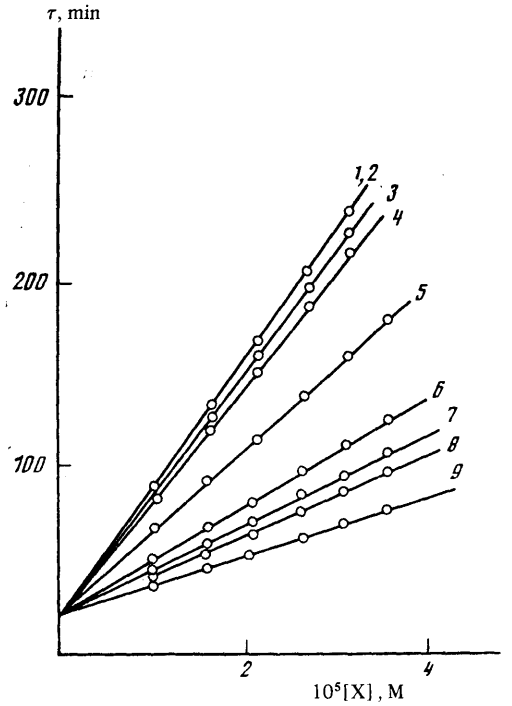


Figure 2. Dependence of the induction period in the polymerisation of methyl methacrylate (τ) on the concentration of inhibitors (60 °C); [ABIN] = 10^{-3} M: (1) S-1; (2) S-47; (3) S-49; (4) S-41; (5) S-789; (6) S-875; (7) HN; (8) HQ; (9) PT.[94]

Another extremely important and objective characteristic of the efficiency of the inhibitor is the stoichiometric coefficient μ. For bifunctional inhibitors such as the S-1, S-41, S-47, and S-49 products, one may expect that in each case μ = 4. However, it was found that in all instances the values of μ found by Eqn.(1) are greater than four. This difference from the theoretical value of μ is associated with the regeneration of the amines as a consequence of the interaction of the inactive inhibitor radical with the growing chain not only via recombination but also via disproportionation. The ratio of these two types of chain termination depends on the structures of both the monomer and the inhibitor. Thus, as a consequence of steric hindrance, the contribution of the recombination reaction in the polymerisation of butyl acrylate is smaller than in the polymerisation of methyl acrylate. This leads to higher values of μ in the inhibition of the polyermisation of butyl acrylate by the above compounds (approximately by a factor of two). Furthermore, the

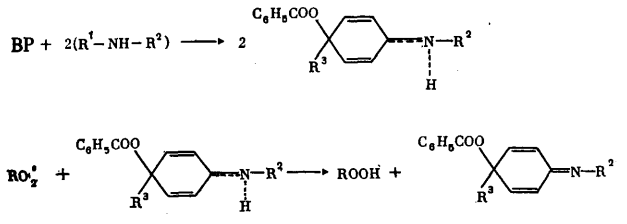
stoichiometric coefficients in the case of both acrylate and methacrylate are greater for S-1 and S-47 than for S-41 and S-49 respectively. The differences between the structures of the amines in each of these pairs are due to the replacement of the benzene ring, linked to the NH group, by the naphthalene ring. In the latter case, the delocalisation of the unpaired electron in the aminyl radical is more significant. This increases the probability of the addition of active radicals not to the nitrogen atom (a process which is sterically hindered) but to one of the carbon atoms of the naphthalene rings, which increases in its turn the contribution of recombination to the overall chain termination.

When the polymerisation process is acted upon by other aromatic amines, also of the polyfunctional type (S-789, S-875, S-933, etc), μ is almost independent of the structure of the inhibiting additive but is determined to a significant extent by the structure of the monomer and the nature of the initiator.[92] In such cases, the active radicals interact with only one NH group, located between two benzene rings. At the same time $\mu \geqslant 2$ also indicates the regeneration of the inhibitor.

The aromatic amines investigated can be arranged in series in terms of their inhibiting activity. For the inhibited oxidative block polymerisation of methyl methacrylate, this series assumes the following form in relation to hydroquinone and phenothiazine:

S-1 > S-41 > S-47 > S-49 > S-789 > S-875 > S-933 > HN > HQ > PT.

In the initiation of the polymerisation of vinyl monomers by benzoyl peroxide (BP), the inhibiting activity of the compounds enumerated above diminishes appreciably. This is caused by the interaction of the peroxide initiator with an amine molecule, which is indicated by the sharp change in the colour of the BP solutions in the monomers when amines are introduced into them. By analogy with the mechanism of the interaction of BP with an arylnitroxyradical,[95] it is assumed[92] that the following reactions occur under the conditions investigated:



Under the real conditions of the synthesis, purification, and storage of acrylic and methacrylic monomers, spontaneous polymerisation frequently occurs and leads to the formation of undesirable high-molecular-wight products. Such polymerisation usually proceeds at elevated temperatures (80–150 °C) in air (naturally in the absence of special initiators) and is thus thermo-oxidative in character. The ballast polymers formed block the industrial apparatus and put it out of order. Furthermore, all this entails considerable losses of the monomers. The search for thermal polymerisation inhibitors in the study of the mechanism of inhibition under these conditions therefore assumes special importance.

The main characteristic feature of the inhibition of the thermal polymerisation of acrylates and methacrylates, in contrast to the initiated polymerisation, is the presence of a break in the dependence of the induction period (at high temperatures) on the inhibitor concentration (Fig.3). From this it follows that there is a critical inhibitor concentration $[X]_{cr}$ above which a sharp increase in the duration of the induction period is observed. The quantity $[X]_{cr}$ then depends significantly not only on temperature but also on the structure of the monomer and the inhibitor.

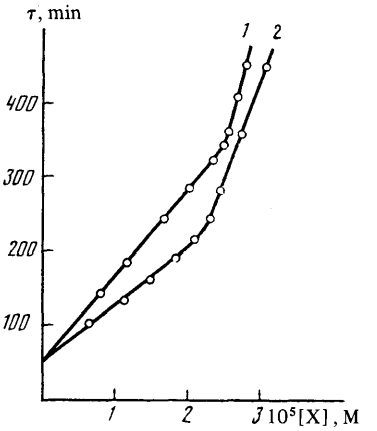


Figure 3. Dependence of the induction period in the thermal polymerisation of methyl methacrylate in air on the concentrations of S-1 (curve *1*) and S-47 (curve *2*) at 100 °C.[94]

For many branched chain reactions, especially for the oxidation of organic compounds, the presence of critical phenomena has been established, including the critical inhibitor concentration.[96,97]

Analogous effects may be observed also in the inhibition of the thermo-oxidative polymerisation of vinyl monomers. The decomposition of polymeric peroxides, leading to the initiation of new reaction centres, occurs also during the induction period and can be regarded as degenerate chain branching. It is noteworthy that degenerate chain branching[98] was not taken into account in any of the previous studies concerned with the inhibition of thermo-oxidative polymerisation.[99–103] These ideas were first put forward in studies[91,92] of the inhibiting capacity of the aromatic amines indicated above.

Kinetic analysis of the radical-chain mechanism of oxidative polymerisation in the presence of inhibitors leads to an equation for the variation of the concentration of polyperoxides (P):

$$\frac{d[P]}{dt} = \nu W_i + \varphi[P], \qquad (14)$$

where $\nu = K_p[M]/\mu K_X[X]$ is the length of the kinetic chain in the presence of the inhibitor, $\varphi = K_3(\nu\alpha - 1)$ the self-acceleration factor, and α the efficiency of the inhibition by polyperoxides.

The condition $\varphi = 0$ is attained at the critical inhibitor concentration $[X]_{cr}$ determined by the rates of chain propagation and decomposition of the polymeric peroxides and also by the occurrence of secondary reactions (for example, the regeneration of the inhibitor):

$$[X]_{cr} = \alpha K_p[M]/\mu K_X. \qquad (15)$$

For $[X] \leqslant [X]_{cr}$, the inhibitor is consumed fairly rapidly inducing only very short induction periods. For $[X] > [X]_{cr}$, the inhibitor concentration diminishes slowly, which leads to a sharp increase in the induction period. The abruptness with which the dependence of τ on [X] passes through $[X]_{cr}$ is determined by the ratio of the rates of initiation and decomposition of polyperoxides (K_i/K_d).

Equations have been obtained[103] for the induction period and for the rate of oxidative polymerisation in the presence of an antioxidant and the lower and upper limits to the inhibitor concentration, the critical rate of initiation, and the critical monomer concentration were established. At inhibitor concentrations below the lower limit, the antioxidant hardly influences the kinetics of the oxidative polymerisation and can be regarded as an inert admixture. Under these conditions, the concept of the induction period is valid only for a reaction taking place in a closed system, while its duration is determined solely by the concentration of oxygen and the rate of its consumption. At inhibitor concentrations greater than the upper limit, the antioxidant acts as an oxidant in relation to the monomer and the polymerisation inhibitor and the concept of the induction period is valid for both closed and open systems. A system passes from the non-inhibited oxidative polymerisation regime to the inhibited reaction regime precisely in the region between the lower and upper limits of the antioxidant concentration.

Extremely interesting phenomena have been observed in the study of the oxidative polymerisation of styrene inhibited by 2,6-di-t-butylphenols.[104,105] The polymerisation kinetics have in these instances a stepwise character, being accompanied by primary (τ_1) and secondary (τ_i) induction periods. The observed kinetics are associated with the period of formation of a secondary inhibitor X^2, whose concentration oscillates as a function of time, i.e. with an auto-oscillatory regime. Since the studies were performed in a closed system, the oscillations in the concentration of the secondary inhibitor are caused, according to the authors, by the involvement of the intermediates in the reaction and are non-decaying in the observed time interval. During the secondary induction periods, the rate of polymerisation decreases sharply with increase in the antioxidant concentration. According to the expression for the induction period in polymerisation in the presence of oxygen,[106,107]

$$\tau = \frac{\mu K_X [O_2]_0 [X]_0}{(K_p [M] + K_X [X]_0) W_i}$$

the latter should be absent at the end of the primary induction period. The role of oxygen in the formation of X^2 should then be indirect and should be shown by the products of the oxidative reaction of phenols. In a general form, the proposed mechanism of the auto-oscillatory regime in the inhibition of the radical polymerisation of styrene includes three main reactions leading to the formation of the secondary products Y and the intermediate Q and to the regeneration of the inhibitor X^2:

$$RO_2^{\cdot} + X^1 \rightarrow Y,$$
$$R + Y \rightarrow Q \rightarrow \text{inactive product},$$
$$Q + X^1 \rightarrow X^2.$$

An attempt has been made[108] to model mathematically the auto-oscillatory polymerisation in the presence of phenols. The main postulate was the idea that polymerisation is then an unbranched radical-chain process (this is in fact achieved at the end of the primary induction period).

2. Inhibition of the Polymerisation of Acrylates and Methacrylates in the Presence of Sulphuric Acid

Sulphuric acid is one of the main components in the synthesis of acrylic and methacrylic monomers. The problem of the inhibition of polymerisation in the presence of sulphuric acid is of particular current interest since the acid is capable of intensifying the formation of polymers and can deactivate many of the known stabilisers.

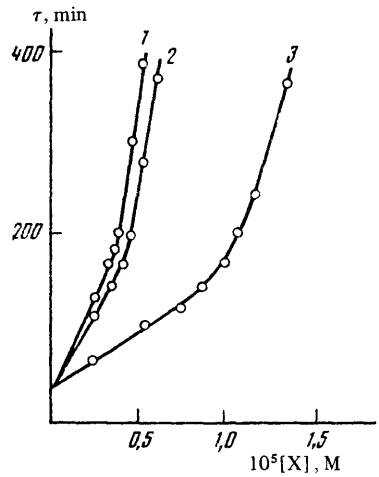


Figure 4. Dependence of the induction period in the polymerisation of methyl acrylate in air in the presence of 5 vol.% of H_2SO_4 on the concentrations of inhibitors at 75 °C: (1) S-1; (2) S-41; (3) HN.[51]

In order to understand the mechanism of inhibition in the presence of sulphuric acid, it is essential to know the specific features of the influence of the acid itself on the elementary polymerisation stages. In the study of the influence of sulphuric acid on the photopolymerisation of methyl methacrylate under oxygen-free conditions,[109–111] the formation of a complex between the acid and the monomer was observed. The increase in the rate and in the degree of polymerisation was explained by the increase in the reactivity of the monomer (or the macroradical) and also by the increase in the macroscopic viscosity and the change in the conformation and in the effective rigidity of the growing chains. The influence of sulphuric acid on the kinetics and mechanism of the polymerisation of acrylic monomers has been investigated[112] at elevated temperatures in the presence of oxygen. The introduction of sulphuric acid decreases sharply the induction period induced by the inhibiting effect of oxygen, and increases the rate of polymerisation. The dependence of the rate and of the induction period on the sulphuric acid concentration has a fairly complex character involving an extremum. The data obtained indicate the formation of complexes between the monomer and acid having different quantitative compositions. The formation of the complex accelerates the decomposition of the peroxide as a result of its protonation by the acid with subsequent homolysis of the -O—O- bond, analogously to the mechanism of the induced decomposition of hydroperoxides in the presence of certain acids.[113]

The compounds listed in Table 1 inhibit effectively the polymerisation of acrylic monomers also in the presence of sulphuric acid.[51,114] With increase in its content in solution, the induction period is sharply reduced, which is associated both with the increase in the rate of initiation and with the interaction of the inhibitor with the acid, lowering its efficiency. In contrast to polymerisation in bulk, where critical phenomena were manifested at fairly high temperatures, in polymerisation in the presence of sulphuric acid they are observed also at relatively low temperatures (Figs.4 and 5).

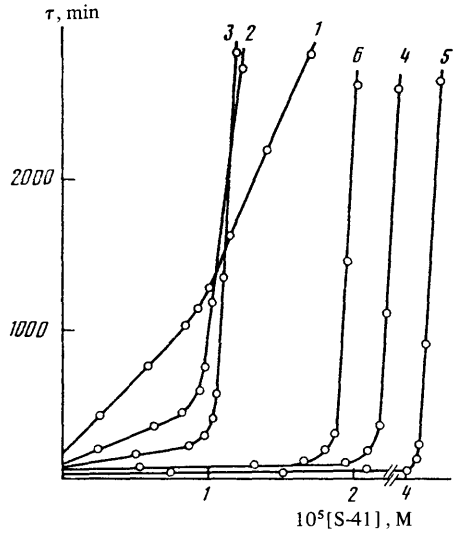


Figure 5. Dependence of the induction period in the polymerisation of methyl methacrylate in air on the S-41 concentration at 60 °C and different initial sulphuric acid concentrations (Vol.%): (1) 2; (2) 5; (3) 10; (4) 20; (5) 30; (6) 41.[51]

Table 2. The critical concentrations of inhibitors in the polymerisation of acrylates and methacrylates in the presence of sulphuric acid.[51]

Inhibitor	$10^5[X]_{cr}$, M, 100 °C	
	methyl acrylate (5 vol.% H_2SO_4)	methyl methacrylate (30 vol.% H_2SO_4)
S-1	0.7	0.8
S-41	0.9	1.3
S-47	—	1.3
S-49	—	1.1
HN	3.0	2.0
HQ	90.0	8.0

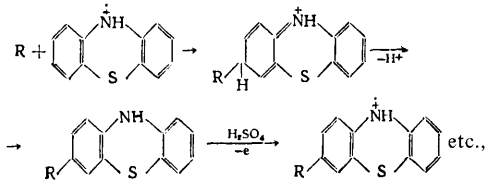
Eqns.(14) and (15) are likewise applicable to the inhibited polymerisation of acrylates and methacrylates in the presence of sulphuric acid. Since the latter accelerates the decomposition of polyperoxides, the observed effects are manifested more strikingly under these conditions. This justifies the view that the critical concentration of the inhibitor can be regarded in such cases as the main parameter characterising the efficiency of the inhibitor. Table 2 presents the values of $[X]_{cr}$ for certain new polymerisation inhibitors and compares them with hydroquinone.

The critical inhibitor concentration, the abruptness with which the dependence of τ on [X] passes through it, and the stoichiometric inhibition coefficient depend on the concentration of the acid in the system. The decrease in μ with increasing concentration of the acid is possible when, as a result of the interaction with it, the substances S-1, S-41, etc. are converted into compounds which either do not inhibit polymerisation or are characterised by a much lower value of μ. A dynamic equilibrium is established between both forms of the substance and an increase in the content of sulphuric acid shifts it towards the less effective inhibitor, which in fact reduces the stoichiometric coefficient.

The EPR spectra of the systems investigated do indeed indicate the interaction of the unpaired electron with the nitrogen and hydrogen atoms, as a result of which the amine (X) is converted into a radical-cation:[51]

$$2X + 3H_2SO_4 \leftarrow 2X^{\dot{+}} + 2HSO_4^- + H_2O + H_2SO_3.$$

Such a reaction had been proposed earlier in a study[115] where an intensification of the inhibiting effect of phenothiazine was observed in the presence of sulphuric acid. The increase in μ was explained by the following inhibition mechanism:



The dependence of the efficiency of the inhibiting effect of the phenothiazine–sulphuric acid system on the acid concentration at a constant phenothiazine concentration passes through an extremum. According to the authors, this is associated with the dual function of sulphuric acid, in the presence of a high concentration of which in the system the initiating effect begins to predominate over the inhibiting effect.

The magnitude of the EPR signal and hence the amount of the radical-cation also vary with the composition of the reaction medium. In sulphuric acid and also in the presence of its excess, the EPR signal is smaller than, for example, in a methyl methacrylate–sulphuric acid solution.

As shown previously,[86] phenols and aromatic amines are used as a rule as antioxidants. On the other hand, in the presence of sulphuric acid the conversion of aromatic amines into stable radical-cations imparts to them the ability to inhibit polymerisation also in the absence of oxygen. At the end of the induction period, polymerisation under oxygen-free conditions proceeds at a steady-state rate, diminishing with increase in the initial inhibitor concentration. This is associated with the retardation of the reaction by the products of the interaction of the active radicals with the amine radical-cations. The kinetic data obtained are consistent with Eqn.(15), which is indicated by the linearity of the relation between $(1-\varphi^2)/\varphi$ and the inhibitor concentration (Fig.6).

The dependence of the steady-state rate of polymerisation on the inhibitor concentration in the presence of atmospheric oxygen has a completely different character. The rate initially increases, but,

having reached a maximum at $[X]_{cr}$, it begins to fall. An increase in the concentration of sulphuric acid in the solution intensifies these effects. The increase in the rate of the process is due to the accumulation of inhibition products—hydroperoxides, the rate of decomposition of which increases in its turn with increasing concentration of the acid. This in fact promotes a more striking manifestation of the extremum in the relation between W and [X] at high acid concentrations. The decrease in the steady-state rate is caused by the consumption of the polymerisation-initiating peroxides and hydroperoxides during the induction period, whose duration increases sharply in the region of $[X]_{cr}$.

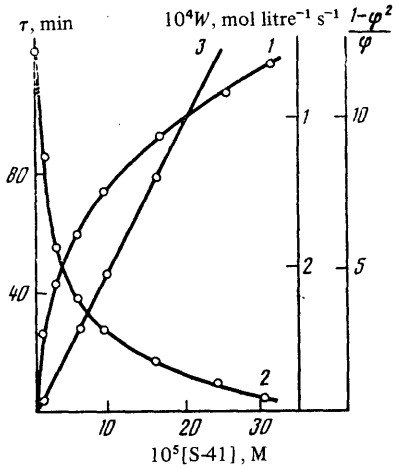


Figure 6. Dependence of the induction period (curve *1*), the steady-state rate of polymerisation of methyl methacrylate (curve *2*), and the ratio $(1-\varphi^2)/\varphi$ (curve *3*) on the concentration of S-41 under oxygen-free conditions and in the presence of 20 vol.% of H_2SO_4; 60 °C; [ABIN] = 2×10^{-4} M.[51]

If initiating products are formed in the inhibition reactions, then this is reflected in the form of the dependence of the induction period on the inhibitor concentration. Indeed, at fairly high concentrations of sulphuric acid, the above dependence deviates from linearity for $[X] < [X]_{cr}$. With increase in the inhibitor concentration, the induction period increases to an increasingly smaller extent and rises sharply only when $[X]_{cr}$ is attained.

V. CHARACTERISTIC FEATURES OF THE INHIBITION OF BULK AND HETEROPHASE POLYMERISATION

The study of inhibition in viscous media makes it possible to simplify greatly the kinetic schemes and to determine in many instances the reactivities of weakly reactive compounds in radical reactions.[17] The principal effect distorting the kinetic picture in polymerisation at relatively high conversions is the gel-effect. In order to control this effect (in order to displace the instant of its appearance to the region of higher conversions or to suppress it completely), one can introduce a relatively ineffective inhibitor into the reaction medium.

In polymerisation in highly viscous media (at high conversions and in systems containing a polymer), quadratic chain termination becomes diffusion-controlled and the constant K_t decreases sharply. In such cases, termination even by a weak inhibitor may become rate-determining and it follows from the expression obtained for the reduced rate

$$\varphi = \frac{W_X}{W} = \frac{(K_t W_i)^{0.5}}{K_X [X]}$$

that the inhibiting effect increases with decrease in K_t and W_i (or with increase in the degree of reaction). Having taken into account the temperature dependence of K_t and K_X, we have

$$\varphi = A \exp[(E_X - 0.5E_o)/RT], \text{ where } A = \frac{A_t W_i^{0.5}}{A_X [X]}$$

Usually $E_X > E_t$ and φ should diminish with increasing temperature, which reduces the gel-effect. Here one should bear in mind that the decrease in φ may be somewhat compensated by the decrease in the inhibition efficiency associated with the increase in K_t as a result of the decrease in the viscosity of the medium as the temperature rises. However, this is observed only when fairly inert products are formed as a result of inhibition.

The decrease in the gel-effect and hence in all the consequences of a high degree of polymerisation can be achieved by introducing oxygen into the reaction system at a specified conversion. At the same time, the most effective inhibition of homopolymerisation at high conversions or under the conditions of a heterophase reaction is observed when oxygen and a weak inhibitor act simultaneously. Calculations for the corresponding radical-chain mechanisms lead in such cases to relations from which it follows that

$$\varphi = W_{O_2}/W = 10^{-3} - 10^{-2},$$
$$\varphi = W_{O_2,X}/W_X = 10^{-6} - 10^{-5}.$$

It is seen from a comparison of these data that oxygen increases the activity of the weak inhibitor. In the presence of oxygen, the intensification of the inhibiting effect of phenols, amines, and nitro-derivatives is associated not only with the formation of their oxidised forms (such as quinones, quinone imines, etc.) but also with the increase in the reactivity of these compounds in reactions with peroxy-radicals compared with the reactions with alkyl radicals.[116]

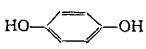
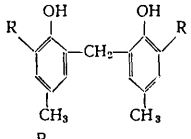
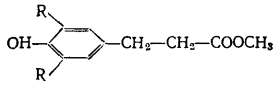
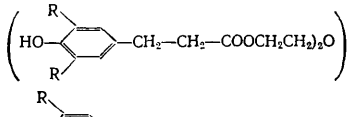
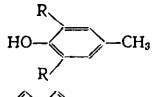
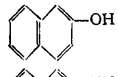
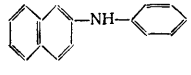
The use of weak inhibitors together with a monomer relatively inactive in relation to copolymerisation is of definite practical concentration interest. If the concentration and reactivity of one monomer are significantly lower than those of the other, then the efficiency of the weak inhibitor increases the degree of conversion more markedly than in the absence of the relatively inactive monomer.

The method of weak inhibition has been used to demonstrate the high activity of certain monomers in copolymerisation reactions.[117]

The characteristic features of the heterophase polymerisation are associated with the low mobility of the macroradicals in the solid phase and with the sharp retardation of the rate of their mutual termination. Under these conditions, the processes involving chain termination by the weak inhibitor may also be significant in the initial stages of the reaction. Therefore in certain cases heterophase polymerisation is a more convenient model for the study of weak inhibition reactions than extensive polymerisation. The efficiency of weak inhibitors in the class of aromatic amines, nitro-derivatives, and phenols increases sharply in the polymerisation of acrylonitrile in bulk compared with the reaction in solution in DMF.[118]

The same effect has been observed in the polymerisation of vinyl chloride and methacrylic acid in bulk and also of methyl methacrylate in the methanol–water precipitating mixture when acted upon by diphenylamine, *m*-dinitrobenzene, and other inhibitors.[119-121] The study of the heterophase polymerisation of various monomers in precipitating media made it possible to obtain data on the reactivites of a large number of inhibitors.[17]

Table 3. The apparent rate constants for the reactions of alkyl (K_X) and peroxy-radicals (K_{XO}) with inhibitors determined during tests (60 °C).[124,126,127]

Inhibitor	Structural formula	10^2K_X; $10^{-4}K_{XO}$, litre mol^{-1} s^{-1}
Hydroquinone		1.8; 21.4
α-Naphthol		1.6; 18.6
22-46		2.1; 39.8
Phenosane 1		0.7; 2.1
Phenosane 28		0.46; 1.7
Ionol		0.7; 2.2
β-Naphthol		0.8; 2.4
Neozone D		0.75; 6.7

Note: R = $C(CH_3)_3$.

The efficiency of weak inhibitors increases in polymerisation emulsion and depends both on their solubility in the chain propagation reaction zone, the topochemistry of the elementary steps, the rate of generation of free radicals, and the number of polymer-monomer species.[122,123]

A series of methods for testing weak radical polymerisation inhibitors, which are strong inhibitors of the oxidative polymerisation and degradation of polymers have been proposed in recent years.[124-127] One of the methods is based on the use of the model reaction involving the heterophase radical polymerisation of acrylonitrile. It is easy to show that the estimation of the apparent inhibition constant K_X in the reaction

$$R + X \rightarrow RH + \dot{X}$$

requires that the following criterion should be satisfied:

$$\frac{W_X}{W} = \frac{(K_i W_i)^{0.5}}{K_X [X]} = \varphi \ll 1.$$

Comparison of data on the inhibition of the polymerisation of acrylonitrile and the inhibition of the oxidative polymerisation and oxidation of hydrocarbons reveal a correlation between the inhibition constants in polymerisation (K_X) and oxidation (K_{XO}) reactions for a series of substituted phenols (Table 3). The correlation makes it possible to predict the reactivities of antioxidants by testing them (in relation to alkyl radicals) with the aid of the model heterophase polymerisation reaction.

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Methods for the Separation and Quantitative Determination of Nucleotides, Nucleosides, and Bases

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The results from the methods for the separation and quantitative determination of nucleotides, nucleosides, and bases† have been classified and discussed. Special consideration has been given to those methods used the most in the last decade—thin-layer chromatography and different types of high-performance liquid chromatography such as ion-exchange, reversed-phase and ion-pair methods, as well as spectrophotometric and titrimetric methods.
The bibliography includes 180 references.

CONTENTS

I. Introduction 1098
II. Thin-layer chromatography 1098
III. High-performance liquid chromatography 1100
IV. Other methods for determining the components of nucleic acids 1105

I. INTRODUCTION

At the present time the separation of the components of nucleic acids is mainly carried out using liquid chromatographic methods such as thin-layer chromatography (TLC) and high-performance liquid chromatography (HPLC); and the number of published studies using these techniques accounts for more than 80% of all the methods used for this purpose.[1,2]

The separation and quantitative determination of components of nucleic acids are very important in different fields of biochemical research and medicine. Components of nucleic acids are to be found in physiological liquids, cells, and tissues.

The presence of these components, their metabolites, as well as modified bases, nucleosides, and nucleotides is used to assess the catabolism of nucleic acids, their fermentative breakdown, and different functional and oncological diseases. No less important is the determination of trace components in commercial preparations of nucleosides and nucleotides. Their use in molecular biology for the synthesis of genetic structures as well as in enzymology as substrates imposes strict requirements for the chromatographic homogeneity of the preparations. Nucleotide analysis is necessary for confirmation of the structure and determination of the quality of chemically synthesised oligonucleotides. A new area in which the analysis of components of nucleic acids is being used is the food industry. Recently, a method for the analysis (using HPLC) of purines and pyrimidines in milk to determine its quality has been posed.[3]

All this indicates that the choice of method and conditions for separation and quantitative determination of the components of nucleic acids are of vital importance at the present time.

In this review we have classified those studies we consider the most interesting during the last ten years on methods for separating bases, nucleosides, and nucleotides such as TLC and HPLC, have indicated the conditions that permit their separation in complex mixtures, focussed attention on their quantitative determination, especially using TLC, and have briefly discussed other analytical methods. The length of this review does not permit a discussion on the problems connected with the preparation of samples for analysis, but they have been reported in detail in two reviews[4,5] and in the literature cited.

II. THIN-LAYER CHROMATOGRAPHY

During the last ten years TLC has become a highly effective analytical method that has been successfully used to solve many problems in different branches of biochemistry, bioorganic chemistry, and molecular biology. The use of modern instruments for quantitative detection and elution, batching systems together with an improved plate quality and development of high-performance thin-layer chromatography (HPTLC) and continuous thin-layer chromatography (CTLC) methods have converted TLC from a qualitative to a quantitative method and have placed it on the same level as HPLC.[6-13]

At the present time TLC has gained universal recognition as a result of the speed of conducting analyses, the relative simplicity of the equipment, its economy and versatility; and with the development of HPTLC, which has considerable advantages over conventional TLC, it has become highly efficient, rapid, sensitive, and reproducible.[14-16] These advantages are achieved with the use of a thin layer of sorbent (silica gel) with uniform particle diameter of about 5 μm, and with new methods for feeding the eluent, the use of special U-chambers for chromatography, an improved method of applying samples, and the use of efficient systems for processing data. The standard deviation of the results in the determination of nanogram quantities of a compound using this method does not exceed 1.5–2.3%. With all these advantages of HPTLC it is possible to separate up to 20 compounds simultaneously over a period of a few minutes and to detect femtogram quantities (10^{-15} g) of compounds.[17]

During the last 5–7 years a new method, CTLC, has been developed, combining the analytical possibilities of TLC and column liquid chromatography.[18] In CTLC the solvent is fed continuously to a thin layer of sorbent with sample previously applied. During separation of the compounds the solvent and compound being

† Referred to as components of nucleic acids in the text.

analysed are continuously removed from the chromatographic system, and at the same time a continuous detection method is carried out. With repeated use of the same plate, constant conditions for separation, complete saturation in the CTLC separation chambers, and a uniform soaking of the sorbent layer it is possible to obtain results with a reproducibility that is better than traditional TLC almost by a factor of 10. Using the continuous method it is possible to separate complex mixtures of compounds (which are separated with difficulty or not separated at all by other methods), and it is a versatile liquid chromatographic method with a very extensive potential for analysis.

A new stage has appeared in the development of TLC—the extensive use of instrumental methods for the quantitative determination of results of separation on a thin layer of adsorbent as well as automation of the whole chromatographic process have started.[17-21] Quantitative analysis in TLC is composed of several stages: introduction of the sample, separation of the components on a thin layer of sorbent, and quantitative determination of the results of analysis. After separation of the compounds on the plate they can be extracted by one of the following methods: removal of the compounds together with the adsorbent layer followed by their extraction; direct extraction from the adsorbent layer bonded to a support with elution by the pumping of an appropriate solvent system through it; extraction of the compounds by addition to the adsorbent layer of a porous material into which they pass together with the solvent; and direct transfer of the compounds being analysed into the detection systems. The methods for quantitative determination of separated compounds can be subdivided into direct and indirect ones. The first group contains all methods that involve the extraction of compounds prior to their quantitative determination. The different methods for analysing extracts and the ranges of detectable quantities of the compounds are shown in Table 1.[22]

Table 1. Methods for the quantitative determination of compounds after their extraction from thin layers of adsorbent.[22]

Quantities determined	1–100 mg	10–100 mg	10–100 ng
Methods of determination	gravimetry, titration, polarimetry	spectrometry, (UV, IR, NMR), mass spectrometry, isotopic methods, GLC refractometry	fluorescence, phosphorescence, biological methods

Extraction of the compounds being analysed together with removal of the adsorbent is carried out manually or by means of automated systems. The adsorbent zone is removed by suction into a suitable tank, from which the compound to be analysed is extracted. For the determination of microquantities of compounds, the adsorbent that is withdrawn into a microtube with solvent is separated by centrifuging or filtration through suitable filters, after which the eluate can be used directly for detection. The volume of eluate usually amounts to 50 – 100 μl and the degree of extraction to more than 90%.[23]

Direct extraction of the compounds being analysed from the adsorbent layer is carried out by preserving the integrity of the layer in the zone itself. The simplest version of this method is one which involves cutting of chromatograms on a flexible support into strips, which are placed in vessels with a solvent to extract the compounds being analysed.[24] A more complete solution to this method consists of the construction of an airtight apparatus and pumping suitable solvent systems through the strips around the zone containing the compound to be analysed. The eluate is then passed to a detection system. The total quantity of solvent passed through varies from 1 to 2 ml and the standard deviation of the results of analysis vary from 0.2 to 1.3% depending on the quantity of compound being analysed.[25] The use of this method is limited by the need for efficient separation of the compounds being analysed.

Simple methods for the direct elution of the separated compounds into microvolumes of solvent (40 – 100 μl) involve the pumping of a solvent through the adsorbent layer containing compound, injecting it on to strips with adsorbent bonded to filter paper, and preliminary concentration followed by elution.[26,27]

When the latter version is used the standard deviation of the results amounts to 0.005 – 0.01 μg.[27] The compounds extracted are detected using spectrophotometric, fluorometric, or radiochemical methods.

The direct quantitative determination of compounds on a chromatogram can be carried out by measuring the area of a spot or its colour intensity. However, this type of determination is associated with significant errors and is only suitable for reference measurements. More accurate methods require the use of special instruments. All the methods of this group are based on the principle of photometry, densitometry being used most frequently followed by spectrophotometric, fluorometric, and radiochemical methods, which have high sensitivity and made identification and quantitative determination possible for a large number of different compounds.[28-32] A comparison of optical methods for the quantitative determination of results from the separation of mixtures is presented in Table 2.[22] Other instrumental methods for the quantitative determination of the results have similar features to the optical methods.

Table 2. Comparison of optical methods for the quantitative determination of results.[22]

Method	Standard deviation, %	Required quantity of compound, μg	Time of analysis, min
Visual comparison	10—30	1—10	0.1
Extraction from layer followed by optical determination	2—5	10—100	20
Optical scanning based on measurements of:			
absorption of radiation	1.5—2.5	0.1—10	2
fluorescence	1—2	10^{-4}—10^{-1}	2

At the present time special equipment used for optical scanning in TLC is still not easy to obtain, as a result of which its widespread application in the laboratory has been somewhat restricted. The most widely used methods of optical scanning have certain limitations—they have insufficiently high chemical selectivity and a restricted area of application. There is a linear dependence of the signal on the content of compound in the zone over a narrow region

of measurement. For this reason the use of these methods for determining impurities at levels of less than 1–2% in preparations of nucleic acid components is virtually impossible.

In optical scanning the nature of sample application, the volume applied, separation, the shape of the spot, and the flow length are decisive factors in obtaining quantitative results. In order to reduce the detection limits, measurements should be made in a transmission system and not a reflection system. With strict adherence to specific conditions the standard deviation of the results of analysis is 1%.

In this connection it is demonstrated that TLC under pressure is a promising method for separating multicomponent mixtures of compounds with similar properties by quantitative scanning.

Radiochemical methods of detection in TLC are characterised by high sensitivity and good reproducibility. Radiochromatograms are evaluated by different methods—directly on the adsorbent layer as well as after extraction of the compound from the layer or by preliminary removal of sections of adsorbent together with the compound being separated. The removal of adsorbent for the analysis of radioactive compounds is carried out using mechanised and automated equipment. The equipment is based on the mechanical scraping off of sorbent and its transfer to the extraction chamber, where desorption of the compounds being determined takes place. The eluate passes through a filter system to collectors and for measurement. The equipment is suitable for the simultaneous analysis of several samples. This method can be used for chromatograms on which the zones of compounds are separated from each other by 2–6 mm.

The detection limit using a radiochemical method is $10^{-7}-10^{-4}$ Ci and depends on the energy of the elementary particles formed by decay of nuclei, the conditions of chromatographic analysis, and the features of the detection system. The standard deviation of the results is 1%. When the samples are analysed there is a linear relationship between the quantity of compound being analysed and the signal of the detection system over a wide range of measurements.[17]

The choice of stationary phase in TLC is decisive in achieving the required selectivity in the separation of mixtures to be analysed. The necessity for highly efficient chromatographic separation presents specific requirements for the choice of adsorbent. Cellulose modified with polyethyleneimine and silica gel have been widely used for the separation of complex mixtures of nucleic acid components. The use of plates with a sorbent layer applied in advance leads to a considerable simplification in the TLC method. Commercial plates provide a better reproducibility of results than with plates prepared in the laboratory because of the high degree of uniformity in composition and thickness of the sorbent. Several firms produce silica gel and polyethyleneimine (PEI)-cellulose plates that are suitable for separation of the components of nucleic acids.[33] The most convenient material as a support is aluminium foil, which can be bent, cut, and made into plates of the required shape. The efficiency of separation depends on the grain size, specific surface area, pore size, and moisture content.[12]

Good separation of compounds occurs on PEI-cellulose when the content of PEI is 0.5–1% and with low pH values of the eluent.[34] The mobility of each product is determined by the magnitude of negative charge, which depends on the pH of the eluent. Boric acid systems are used to separate deoxyribo- and ribo- derivatives. Borate complexes of ribonucleotides have an additional negative charge and have lower mobility than deoxyribo- derivatives. Multistep or gradient elution with salt solutions of varying concentration is used to separate compounds according to the number of their phosphate groups.[35–39] The separation of uncharged compounds—purine and pyrimidine bases and nucleosides—is carried out on unmodified cellulose or silica gel.

Silica gel is used to separate different mixtures of components of nucleic acids. The selection of suitable solvent systems permits separation with respect to both the type of nitrogenous base and the type of carbon residue.[40–44] Good separation of complex mixtures containing 5′- and 5′-poly-phosphates of purine nucleosides occurs with the use of systems containing ammonia as a strong base, which prevents the formation of hydrogen bonds between the amino groups of the compounds being analysed and silica gel. For the separation of nucleoside 5′-polyphosphates, acidic systems containing isobutyric acid are the most suitable; for nucleosides the most suitable are "reversed-phase" systems having a high concentration of salts such as $(NH_4)_2SO_4$ and NaCl.

For the separation of components of nucleic acids silica gel has been successfully used in recent years in HPTLC, which is characterised by highly efficient separation and a low detection limit for compounds. With the use of adsorbents such as aminopropylated silica gel, which has anion-exchange properties, and silica gel modified with hydrocarbon radicals, a number of studies have been carried out on the separation of components of nucleic acids.[45–53]

The best results on the separation of complex mixtures of nucleic acid components that differ according to the type of nitrogenous base, hydrocarbon residue, and number of phosphate groups have been obtained using two-dimensional chromatography and mainly on PEI-cellulose.[54–57] Some data on the separation of different mixtures of components of nucleic acids are presented in Table 3.

III. HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

The progress made using HPLC is due to its high resolving power, mild conditions for separation, and efficient design of apparatus. The use of high-pressure chromatographs with high-sensitivity detectors, new types of sorbent, and also the design of spectrophotometers that permit ultramicroanalysis to be carried out have contributed towards providing HPLC with a lead over all other methods in its use for the separation of components of nucleic acids and has made it possible to separate effectively microgram and nanogram quantities of compounds in a short time.[61–68]

A general tendency in HPLC is the change-over to the use of chemically modified silica gels as sorbents with particle diameter of 5–10 μm and even 3μm. Detection is carried out using fluorescence, UV-photometric, electrochemical, or atomic emission detectors,[68–77] while identification of the components can be carried out using a combination of HPLC and mass spectrometry.[78–80]

For the separation of components of nucleic acids, those forms of HPLC such as ion-exchange chromatography, reversed-phase chromatography and ion-pair reversed-phase chromatography are used almost exclusively. Adsorption ("direct-phase") HPLC is used at the present time only in isolated cases.[81]

1. Ion-exchange High-performance Liquid Chromatography

Ion-exchange chromatography (IEC) is a traditional method for separating the components of nucleic acids.[34,65,82] In ion-exchange chromatography, separation of the compounds is based on the difference in charges on their molecules; hydrophobic interactions also play a definite part. At the present time a large number of different ion exchangers for HPLC are produced. Generally, these

Table 3. Separation of the components of nucleic acids by thin layer chromatography.

Components separated	Adsorbent	Solvent systems	Note	Refs.
Bases, deoxyribonucleotides deoxyribonucleosides	silufol (Kavalier, Czechoslovakia)	dioxan–isopropanol–2 M ammonia–1 M ammonium acetate (3:2:4.7:0.3); dioxan–isopropanol–5 M ammonia–1 M ammonium acetate (3:1.8:4.9:0.3)	–	[44]
Bases, deoxyribonucleosides	silufol (Kavalier, Czechoslovakia)	dioxan–ammonia (7:3); isopropanol–ammonia (8:2); dioxan–isopropanol–ammonia (4:4:2)	radiochemical detection	[44]
	RP-silica gel C_{12} (Kodak, USA)	1.5 mM TBA + 5% methanol; 0.4 M ammonium phosphate, pH 3.5; 0.1 M ammonium acetate, pH 6.9 + 5% acetonitrile		[51]
Ribonucleotides	NH_2-silufol	1 M acetic acid–ethanol (10:1), pH 3.2	–	[52]
Bases, ribo- and deoxyribo-nucleosides and nucleotides	silica gel GF-254 (HPTLC), (Merck, FRG); PEI-cellulose (Merck, FRG)	Chloroform–methanol–acetic acid (3:2:1); chloroform–methanol–water (81:15:4)	nucleotides remain at start	[58]
		Chloroform–methanol–acetic acid (3:2:1) in 0.1 M boric acid		[58]
Ribo- and deoxyribo-nucleotides	PEI-cellulose (Merck, FRG)	0.25 M acetic acid (9 cm), 0.8 M formic acid (4 cm)–direction 1; 0.22 M Tris-HCl, pH 8.0, in methanol (10 min), methanol (10 min)–direction 2	two-dimensional chromatography	[59]
Ribonucleotides	PEI-cellulose (Merck, FRG)	direction 1–0.2 M LiCl (2 min), 1 M LiCl (6 min) 1.6 M LiCl (75 min); 0.5 M sodium formate, pH 3.4 (0.5 min) 2 M sodium formate, pH 3.4 (2 min), 4 M sodium formate, pH 3.4 (60 min)–direction 2	two-dimensional chromatography	[59]
Ribonucleoside 5′-mono-, 5′-di-, and 5′-tri-phosphates	silufol (Kavalier, Czechoslovakia)	dioxan–isopropanol–water–ammonia (4:2:4:1); dioxan–water–ammonia (6:4:1)	radiochemical detector	[43]
		dioxan–isopropanol–ammonia–1 M ammonium acetate (3:2:4.7:0.3)		[44]
	NH_2-silica gel (HPTLC), (Merck, FRG)	0.2 M NaCl in a mixture of: methanol–water (3:7); 0.2 M NaCl mixed with methanol, ethanol, and chloroform		[47]
Deoxynucleoside 5′-mono-5′-di- and 5′-tri-phosphates	NH_2-silufol	1 M acetic acid–ethanol (10:1), pH 6.5	radiochemical detector; two-dimensional chromatography	[52]
	NH_2-silufol	1 M acetic acid–ethanol (10:1), pH 6.5		
Ribo- and deoxyribo-nucleoside 5′-triphosphates	PEI-cellulose (Merck, FRG)	direction 1—1 M LiCl with 5% boric acid, pH 7.0, washing with methanol, 2 M sodium formate (pH 3.4)–1.6 M LiCl (1:1) at 4 °C; 0.85 M potassium phosphate, pH 3.4—direction 2	"	[60]
Ribo- and deoxyribo-nucleosides	cellulose (Merck, FRG)	0.2 M; 2 M; saturated solution of $(NH_4)_2SO_4$	"	[35]

are either modified copolymers of styrene with divinylbenzene containing a relatively high proportion of the latter or supports based on microporous silica gels.[83] Anion exchangers usually contain quaternary ammonium groups (Partisil-10 SAX, Ultrasil-10 AX, Lichrosorb AN, etc.), less often they contain tertiary amino groups (Nucleogen DEAE). Quite often aminopropylated silica gel (APS-Hypersil, Lichrosorb-NH_2) is used as an anion exchanger. The advantage of ion exchangers based on silica gel is the highly effective separation and short analysis time achieved by high rates of mass exchange, although the stability of these sorbents is not high and the operating pH range for the mobile phase is from 2 to 7.5.[59–63,83–85] Cation exchangers most frequently contain alkylsulphonate groups (Partisil-10 SCX, Ultrasil-10 CX). In recent years ion-exchange derivatives of rigid hydrophilic resins such as Spherone, TSK-Gel-PW,[84] and others have been used quite frequently.

Anion-exchange chromatography is widely used for the analysis of nucleotides, in particular, nucleoside polyphosphates.[86–97] Gradient elution is more frequently used. Although this permits separation of more than 20 compounds over a short period of time, much time is spent in regenerating the column after analysis. Moreover, the salt concentration gradient leads to a drift in the base line of the UV detector. The drift can be compensated by the addition of a calculated quantity of acetone to the initial buffer or by partial replacement of phosphate by chloride, inclusion of which in the mobile phase can, however, lead to corrosion of the chromatographic equipment.[98–100]

An isocratic system of separation does not impose such high requirements of purity for the reagents being used and gives better reproducibility of results than with gradient elution. A disadvantage of isocratic chromatography is the appreciable width of peaks with large K' values for retention of the chromatographic zone, which reduces the sensitivity and accuracy of analysis.[101,102]

The order of elution of nucleotides during anion-exchange HPLC is not always easy to interpret. Perhaps the only rule that has no exceptions is the order of elution of nucleoside polyphosphates: NMP, NDP, NTP.‡ It is a more complex problem with isomeric nucleoside monophosphates and with the separation of ribo- and deoxyribo-nucleotides. Thus, Nguyen and co-authors[102] observed the following orders of elution (column with Partisil-10 SAX sorbent, 3% MeOH in 0.08 M phosphate buffer as eluent, pH 4.15):

1) CMP, UMP, AMP, GMP
2) dCMP, TMP, dAMP, dGMP
3) 2′-UMP, 2′-AMP, 2′-CMP, 2′-GMP,
4) 3′-UMP, 3′-CMP, 3′-AMP, 3′-GMP
5) dCMP, CMP, 3′-CMP, 2′-CMP
6) UMP, 2′-UMP, 3′-UMP
7) AMP, dAMP, 3′-dAMP, 2′-AMP, 3′-AMP
8) 3′-dGMP, GMP, dGMP, 3′-GMP, 2′GMP.

‡ Abbreviations for the components of nucleic acids are given in accordance with the IUPAC–IUB recommendations (Molekulyar. Biolog., 1972, **6**(1), 167–171).

As can be seen, the pattern is very complex. It is clear that hydrophobic interactions do not play a conclusive role. Although adenine is protonated to a considerable degree at pH 4.15, adenine nucleotides are eluted after UMP and TMP. At lower pH values, however, AMP "overtakes" UMP, but the order of UMP and GMP is retained.

Bases and nucleosides are separated on anion exchangers as a result of hydrophobic interactions. Non-ionic interactions with the support are partly suppressed by an increase in temperature and the addition of organic solvents to the mobile phase.[103,104] With an isocratic system it is possible to separate bases, nucleosides, and nucleotides simultaneously.

Recently, the need to speed up and simplify analyses and also the necessity for analysing very complex samples containing bases, nucleosides, and their mono- and poly-phosphates as well as UDPG, NAD, NADP, and related compounds have led to a certain decline in interest in anion-exchange chromatography and have stimulated research in the field of ion-pair RPC (see below). Combined chromatographic systems that consist of two anion-exchange and reversed-phase columns are also capable of separating such mixtures effectively, but the method of analysis in this case is considerably more complex.[105,106]

As regards cation-exchange chromatography, this method has been used traditionally for the analysis of bases. Taking into account the fact that at low pH values the charge of bases differs by no more than one, separation can readily be carried out in an isocratic system. Examples of the separation of components of nucleic acids are given in Table 4.

2. Reversed-Phase Chromatography

Chromatography in which the eluent is more polar than the stationary phase is known as reversed-phase. Usually the stationary phase is in the form of a silylalkyl ether, while aqueous buffer solutions and/or their mixtures with polar organic solvents are used as the mobile phase.[108] The widespread use of RPC is due to a whole number of advantages:[108,109] a) compounds of very diverse classes can be separated, and compounds that have marked differences in polarity and structure can be separated in one chromatographic cycle (for example, a mixture of nucleosides and their phosphates); b) the method has high efficiency and selectivity; c) the columns are rapidly regenerated; d) the method can be used to analyse very dilute samples with a large volume; e) the supports are commercially available.

The following disadvantages of the RPC method should be mentioned:[108] a) the stationary phases are only stable over the pH range 2–7.5; b) interaction of the molecules being separated with the stationary phase has a composite mechanism because of the presence of residual silanol groups (Si–OH) on the surface of the stationary phase; c) the retention mechanism of compounds in RPC has been insufficiently studied. Evidently these shortcomings are not fundamental problems and it is nearly always possible to select the optimum combination of stationary and mobile phases for the resolution of any given task.

Microporous silica gels with chemically bonded hydrocarbon groups, most frequently n-octadecyl (C_{18} or ODS) or n-octyl groups (C_8), are used in RPC as stationary phases.[109] In order to obtain them, silica gels are usually treated with alkylsilyl halides. However, because of steric hindrance, up to 30% of the silanol groups present on the surface of the silica gel remain unmodified; a limited portion of them can be removed by repeated treatment, with trimethylsilylating agents, and by "capping".[109–111] The properties of the stationary phases depend on the type of grafted ligand, the concentration of alkyl and available silanol groups on the surface, the characteristics of the initial silica gel, the specific surface area, the specific pore volume, etc.[110–120]

In one review[108] there is a list of more than 70 supports, which were being produced by over 50 firms. It may be assumed that by now the number of supports being produced has increased even further.

Table 4. Examples of the separation of components of nucleic acids by ion-exchange HPLC.

Sample No.	Type of sample	Support*; column dimensions, mm	Composition of mobile phase and type of elution	Order of elution of sample components	Complete analysis time, min	Refs.
1	synthetic mixture	TSK gel K-anion-BW (9 μm); 0.19×450	80 μM $(NH_4)HPO_4$, pH 7.15	Cyd < Urd < Cyt < Ura < Guo < Ado < Gua < Ade < CMP < UMP < 2′-CMP < 3-CMP < 2′UMP < 3′-UMP < GMP < AMP < 2′-GMP < 2-AMP < 3′-GMP < 3′-AMP	60	[87]
2	synthetic mixture	Partisil 10-SAX (10 μm); 4.6×250	Gradient up to 0.3 M KH_2PO_4 and 0.3 M KCl, pH 3.3 → 4.9	CMP < AMP < UMP < IMP < GMP < UDP < CDP < ITP < CTP < ATP < GTP < NADH < NADPH < UDPG	~40	[94]
3	cellular extracts	APS-Hypersil (5 μm); 5.0×100	Gradient up to 0.5 M KH_2PO_4 and 0.8 M KCl, pH 2.9	XMP < CMP < AMP < NAD^+ < TMP < IMP < GMP < CDP < UDPG < ADP < dADP < TDP < GDP < CTP < ATP < dATP < GTP	~15	[95]
4	rat liver extract	Lichrosorb-NH_2 (5 μm); 4.6×150	0.1 M K_2HPO_4, 0.1 M NH_4Cl, 20% MeCN, pH 6.5	AMP < GMP < $NADP^+$ < ADP NADPH < GDP < ATP < GTP	20–25	[106]
5	DNA hydrolysates from fibroblast cultures	Ultrasil-10CX (10 μm); 4.6×250	0.02 M $(NH_4)H_2PO_4$, pH 2.3	Thy < Gua < Cyt < Ade < m^5Cyt	~15	[107]

* Particle diameter given in brackets.

The lack of information on their method of synthesis and properties produces a certain difficulty in operating with commercial supports. It is therefore not surprising that a comparative study of the chromatographic properties of commercial supports has been the subject of a large number of studies, the results of which can be reduced to the following principles:[121-129]

1. In the RPC of nonpolar compounds the selectivity of separation does not depend very much on the type of support and the efficiency also does not vary significantly.

2. The separation of compounds containing polar groups is affected not only by the type of support but also by the difference in batches of supports of a single type. In this case asymmetry and/or broadening of the chromatographic peaks often occur, which is usually due to the presence of available silanols on the surface and its contamination with heavy metals.

3. Supports with a high content of residual silanols (Nucleosil-C_8, Partisil-ODS2, Partisil-ODS3) have inferior stability in aqueous salt mobile phases compared to capped supports (Nucleosil-C_{18}, Partisil-CDS_3, CCS-C_8, Ultrasil-ODS, and others) because of the more rapid dissolving of the silica gel matrix and the possible irreversible adsorption of different compounds.

Reversed-phase chromatography is a most important and widely used method for separating the components of nucleic acids that is based on the high selectivity of nonpolar supports with respect to heterocyclic bases.[130-140] In studies on the effect of RPC parameters on the separation of components of nucleic acids it was found that the content of the organic solvent in the mobile phase does not alter the selectivity of separation but only affects the retention; the pH and ionic strength can affect the selectivity of separation.[129-131]

Bases and nucleosides can be separated using RPC with low concentrations of organic solvents. In order to suppress nonspecific interactions a buffer (usually phosphate, pH 4–6) is added in low concentration (10–50 mM) to the eluent. As can be seen from Table 5, bases are eluted first, then the corresponding nucleosides, and finally deoxynucleosides, with purines usually being retained to a greater extent than pyrimidines. In solving frequent problems the analytical method can be simplified by varying the composition of the mobile phase. Thus, Fraser and Pearson[141] carried out the separation of a mixture at pH 2.5. In this case dU and T were effectively separated, while dA, dG, and dC, which were not of interest to the authors, were hardly retained at all on a reversed-phase column.

Clinical samples and also hydrolysates of tRNA can contain up to 20 minor nucleosides, so analysis of such complex samples requires the use of gradient elution (Nos.1–3, Table 5). The problems associated with the analysis of minor nucleosides in the clinic have been examined in detail in two reviews[4,5] and in one study[133] where the authors succeeded in separating and determining quantitatively more than 20 nucleosides in samples of physiological origin. Elution was carried out in a multistage MeOH gradient and the analysis time amounted to over 100 min. For the analysis of a less complex sample the same authors used isocratic elution; the analysis time was reduced by a factor of nearly 15. Examples of the separation of bases and nucleosides are given in Table 5.

The presence of a negatively charged phosphate group makes nucleotide molecules more hydrophilic than molecules of nucleosides and bases, so that nucleotides are retained to a lesser degree on reversed-phase columns. Mobile phases without organic solvents are used for the separation of nucleotides; the pH is most frequently about 4–5, which suppresses the ionisation of a second phosphate group, and the concentration of buffer is increased considerably in comparison to the RPC of nucleosides.

An increase in the ionic strength of the mobile phase leads to an increase in retention time of nucleotides to acceptable values during RPC (this effect has been studied in detail[97,129,130]), while at the same time because of the increase in inherent UV absorption of the mobile phase the sensitivity of the detector is reduced.

Nucleoside polyphosphate molecules are even more hydrophilic. The order of elution for polyphosphates (NTP < NDP < NMP) in RPC is the reverse of that in anion-exchange chromatography.

When the simultaneous separation of nucleotides and nucleosides in the mobile phase is required, methanol must be added and gradient elution carried out.[147-150]

Examples of the separation of nucleotides are given in Table 6.

Table 5. Examples of the separation of bases and nucleosides by reversed-phase HPLC.

Sample No.	Type of sample	Support; column dimensions, mm	Composition of mobile phase and type of elution	Order of elution of sample components	Complete analysis time, min	Refs.
1	clinical analyses	Ultrasphera-ODS (5 μm); 4.6 × 150	MeOH gradient, 10 mM KH_2PO_4, pH 4.9	Hx < dCyd < Ado < Ino < dGuo < Thd < Ade < dAdo	25	[142]
2	clinical analyses	Hypersil-ODS (3 μm); 4.6 × 50 + 4.6 × 150	MeOH gradient, phosphate buffer, pH 6.0	Cyt < Ura < Cyd < Hx < Xan < Urd < Ade < Ino <	~20	[143]
3	tRNA hydrolysates or tissue extracts	μ-Bondapak C_{18} (10 μm); 4.0 × 300	MeOH gradient, phosphate buffer, pH 5.1 (36 °C)	Guo < dUrd < dCyd < Thd < Ado < dAdo Cyd < Urd < m^1Ado < m^5Cyd < m^7Guo—about 15 nucleosides in all	35-40	[144]
4	DNA and RNA hydrolysates	Supelcosil C_{18}-DB (5 μm); 4.6 × 150	8% MeOH in 0.05 M KH_2PO_4, pH 4.0	Cyd < dUrd < dUrd < m^5dCyd < Ino < Guo < dIno < dGuo < dThd < Ado < dAdo	7	[145]
5	human placental extract	Micropak CH-10 (10 μm); 4.0 × 300	MeOH gradient, phosphate buffer, pH 6.5	Xam < Hx < NAD^+ < Ino < Ado < Ade	~20	[146]

Table 6. Examples of the separation of nucleotides by reversed-phase HPLC.

Type of sample	Support, column dimensions, mm	Composition of mobile phase and type of elution	Order of elution of sample components	Complete analysis time, min	Refs.
Bacterial cellular extracts	μ-Bondapak C_{18} (10 μm); 4,0×300	0,2 M $(NH_4)_2HPO_4$, pH 5,1	GTP < GDP < ATP < ADP < AMP	<20	[119]
Extracts of erythrocytes, hepatocytes, and different tissues	LiChrospher 100 CH-18 (5 μm); 4,0×250	Phosphate buffer, pH 6.0; gradient up to 7.5% MeCN	GTP < GDP < GMP < IMP < ATP < ADP < Urd < AMP < $NADP^+$ < NAD^+ < Guo < Ado	30—40	[131]
Products of the chemical phosphorylation of nucleosides	Ultrasphere-ODS (5 μm); 4,6×250	10% MeOH, 0,05 M $(NH_4)H_2PO_4$	AMP < 2′-AMP < Ade < 2′, 3′-cAMP < 3′-AMP < 3,5′-cAMP < Ado	10—20	[140]
DNA and rat liver hydrolysates	Spherisorb-ODS (10 μm); 4,6×500	0.5 or 0.75 M Na_2HPO_4, pH 5,5	dCMP < m^5dCMP < TMP < dGMP < dAMP	~125	[147]
Human liver extracts	Spherisorb-ODS (10 μm); 4,6×500	25 mM NaH_2PO_4 pH 5,5	ATP < ADP < AMP < $NADP^+$ < NAD^+	120	[151]

3. Ion-Pair Reversed-Phase Chromatography

Ion-pair (IP) reversed-phase chromatography (RPC) is a form of RPC used to separate compounds that dissociate in aqueous organic solvents. Compounds containing lipophilic groups capable of forming ion pairs with ions of the opposite charge from the components of the sample being analysed are added to the mobile phase; the compounds are sodium dodecylsulphate, quaternary ammonium bases or zwitterions.[152–154]

As has already been stated, nucleotides, in particular nucleoside polyphosphates, are only weakly retained on reversed-phase sorbents because of their low hydrophobic capacity. There are two methods of increasing the retention of ionised molecules during RPC. Firstly, chromatography can be conducted with that pH of eluent at which the acid (or basic) dissociation of the molecules of compound being separated is insignificant. This method, often called "ion suppression",[155] in relation to nucleotides is to a certain extent used in those studies that were discussed in the previous section. Secondly, nucleotides are suitable candidates for IP RPC; in this case an increase in retention of the ions is achieved by introduction of hydrophobic ions of the opposite charge into the mobile phase.

A number of studies[155-157] have been devoted to studying the mechanism of IP RPC. We can list here the main conclusions of these investigations:

1. The presence of hydrophobic ions in the mobile phase strengthens the adsorption of ions of the opposite charge. The more hydrophobic the ion, the greater is the increase in K' for the counter-ion. Consequently, the effect occurs at lower concentrtions for a more hydrophobic ion. Thus, addition of 2.5 mM TBA to the mobile phase increases K' for the nucleotides to a greater extent than addition of 5 mM TEA or 20 mM TMA.[158]

2. The dependence of K' on the concentration of hydrophobic counter-ion for ionic components of a mixture most frequently follows a bell-shaped curve; nucleotides are no exception to this rule.[159] The position of the K' maxima varies somewhat for different compounds under the same conditions. As a rule, the concentration of ion-pair agent is selected in the region of K' maxima of the components of the mixture being separated.

3. The presence of hydrophobic ions in the mobile phase slightly reduces the retention of nonionic compounds; for example, addition of TBA to the eluent reduces the K' values of nucleosides.[159]

4. As in conventional RPC, an increase in the concentration of organic solvent decreases the retention time of both ionic and nonionic components in IP RPC.

5. An increase in the concentration of salts reduces the retention time of ionic components in IP RPC.

6. The relationship between retention times and pH in IP RPC is the reverse of that with ion suppression; the retention time is longer if the eluate molecules are ionised and capable of forming an ion air. Thus, at pH 3.0 addition of TBA increases K' for TMP and UMP and has no effect on K' for CMP and AMP, which at pH 3.0 are zwitterions; at pH 5.7 TBA increases K' for all nucleotides.[160–162]

We should mention that the actual mechanism of IP RPC has not so far been established. Hypothetical "ion-pair", "dynamic ion-exchange", and "ionic-interaction" mechanisms have been discussed in one review.[155]

Some examples of the analysis of components of nucleic acids using IP RPC are given in Table 7. We have restricted ourselves here to five examples but the number of studies on the IP RPC of nucleotides is very considerable.[152,163–169]

The order of elution of nucleoside polyphosphates is the same as that in anion-exchange chromatography. It is interesting to note that in 2.5 mM TBA the order of elution of mononucleotides also corresponds to the order of elution in anion-exchange chromatography at low pH. In 20 mM TMA, UMP is eluted after CMP, as in normal RPC.

In all of the examples in Table 7 apart from No.4, an isocratic system of elution was used, although in some cases nucleoside polyphosphates with considerable different molecular charges were separated, in other cases nucleotides and nucleosides were separated. On the whole, gradient elution is used less often in IP RPC than in ion-exchange chromatography or in RPC for mixtures of nucleosides and nucleotides, which is a definite advantage.

As was mentioned above, for the analysis of very complex samples either quite elaborate systems combining IEC and RPC are used or IP RPC is used, and this is illustrated by example No.4 in Table 7.

Table 7. Examples of the separation of components of nucleic acids by IP RPC.

Sample No.	Type of sample	Support; column dimensions, mm	Composition of mobile phase and type of elution	Order of elution of sample components	Complete analysis time, min	Refs.
1	Various tissue extracts	Lichrosorb RP-8 (RP-18); 4,0×250	0.3% TBA; 0.65 KH_2PO_4, pH 5.8; 240 ml MeCN, water up to 1100 ml	AMP < ADP < GTP < UTP < ATP	~10	[155]
2	Various tissue extracts	Ultrasphere ODS (5 μm); 4,6×250	2,5 мМ TBA; 12% MeCN pH 2,5 (HCOOH)	CMP < AMP < GMP < UMP < IMP < XMP	~30	[158]
3	Hydrolysates of chemically synthesised oligonucleotides	Partisil-5C_8; 5 (μm) 4,6×250	2.0 мМ TBP; 0.005 М KH_2PO_4, pH 4,9; 7% MeOH	dCyd < dCMP < dGuo < Thd < dGMP < TMP < dAdo < dAMP <	~60	[159]
4	Various mixtures	Servachrom ODS-S: 100; 4,6×250	5.0 mM TBA; phosphate buffer, pH 6.0; gradient up to 10% MeCN	Cyd < Urd < CMP < Guo < UMP < GMP < Ado < CDP < AMP < UDP < GDP < CTP < ADP < UTP < GTP < ATP	~60	[170]
5	DNA hydrolysate	Ultrasphere-C_8 (5 μm); —	10 mM hexanesulphonate; 5% MeCN; 10 mM phosphate buffer, pH 2.9	Ura < Hx < Guo < Cyt < m^5Cyt < Ade	10	[171]

Although the separation in example No.4 is not so impressive as in two studies,[105,106] it was obtained in a considerably simpler system, and it may be assumed that separation of a 16-component mixture is within the limits of IP RPC, especially when gradient elution is used.

Finally, nucleic bases can also be separated at low pH values under conditions of IP RPC by introduction of suitable components to the mobile phase (see, examples No.5, Table 7 and No.5, Table 4).

Thus, ion-pair chromatography is the most promising method of HPLC for the analysis of nucleotides or their mixtures with nucleosides.

IV. OTHER METHODS FOR DETERMINING THE COMPONENTS OF NUCLEIC ACIDS

In the last 8–10 years there has been a development of methods for potentiometric titration of components of nucleic acids based on the acid-base properties of purine and pyrimidine bases, methods based on the selective oxidation of the *cis*-1,2-glycol group of the ribose part of ribonucleosides and their phosphates, and methods based on colour reactions of purine bases and the carbon part of the nucleosides.

For the separate analysis of multicomponent mixtures of nucleic acid components, differential alkalimetric or acidimetric titration in the medium of organic solvents is used without requiring preliminary separation of the different purine and pyrimidine derivatives.[172-174]

Potentiometric titration methods are specific and accurate. The disadvantages in using them relate to the large consumption of samples (20–200 mg) and the impossibility of determining impurities that constitute less than 10%.

In order to make a selective determination of ribonucleosides and their phosphates, methods for the oxidation of the *cis*-1,2-glycol group with periodate are used with subsequent titrimetric or colorimetric analysis of the iodate formed by oxidation of the compounds being analysed.[175-176]

The colour reactions used to determine the components of nucleic acids are based on the following properties: adenine is diazotised to give azo compounds with α-naphthylamine; guanine is reacted with Folin's reagent; purine nucleotides form coloured ribose compounds with orcein and deoxyribose compounds with diphenylamine.[177-180]

Methods for oxidation of the *cis*-1,2-glycol group in ribose and the colour reactions which are used to determine the components of nucleic acids are selective and sensitive and are used for the analysis of a specific class of compounds, but they are not suitable for the differentiated determination of nucleic acid components within this class.

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Modern Ideas About the Mechanisms of Homogeneous and Heterogeneous Acid Catalysis: Similarities and Differences

V.B.Kazanskii

The modern ideas about the nature of the protonated states in aqueous solutions in non-polar solvents and on the surfaces of heterogeneous oxide catalysts of the acid type are examined. It is concluded that in heterogeneous systems mechanisms analogous to the mechanism of homogeneous acid catalysis in aqueous solutions operate only in catalytic reactions of polar molecules. Owing to the absence of solvation effects, the catalytic reactions of hydrocarbons take place, contrary to the widely held view, via intermediate covalent and not ionic structures. On the other hand, the properties of carbenium ions are characteristic of transition states, which in many instances also possess features resembling those of adsorbed carbenes of surface ylides. The role of synchronous or concerted mechanisms in heterogeneous acid catalysis is discussed.
The bibliography includes 108 references.

CONTENTS

I.	Introduction	1109
II.	Homogeneous acid catalysis	1110
III.	Heterogeneous acid catalysis	1113
IV.	Conclusion	1121

I. INTRODUCTION

The phenomenon of acid catalysis consists in the acceleration of chemical reactions in the presence of liquid (homogeneous acid catalysis) or solid (heterogeneous acid catalysis) acids. Individual examples of acid catalysis were known very long ago, as early as the end of the XVIIIth century. They include, for example, the esterification of alcohols, the hydration of olefins, etc.

Heterogeneous acid catalysis, with the aid of which the majority of the reactions in petrochemistry and petroleum processing (cracking and skeletal isomerisation of paraffins and olefins, the migration of the double bond in olefins, their oligomerisation, the alkylation of aromatic compounds, etc.) are nowadays carried out, has found the widest practical applications. The explanation is that heterogeneous acid catalytic reactions can be carried out over a wide temperature range, up to 700–800 K, which naturally extends the range of thermodynamically feasible catalytic reactions. Furthermore, heterogeneous catalysis is more susceptible to technological formulation, since it is easier to achieve on its basis continuous chemical manufacturing processes in which there is no stage involving the separation of the catalyst from the initial reactants and the final products.

The examples of the practical use of homogeneous acid catalysis are much more modest. Perhaps the most important of these is the alkylation, on a large industrial scale, of isoparaffins by olefins, and the hydration of ethylene in the presence of sulphuric acid. Despite

this, the ideas about the mechanisms of acid catalysis were formulated as early as the late 1920's precisely for homogeneous catalysis. We shall therefore begin the consideration of the mechanism of acid catalytic reactions with homogeneous catalysis.

II. HOMOGENEOUS ACID CATALYSIS

1. Catalysis in Aqueous Solutions. The Brønsted Relation

The theory of homogeneous acid catalysis in aqueous solutions, formulated in 1924 by Brønsted,[1,2] is based on the idea of the intermediate protolytic interaction of the reactants with the undissociated acid molecules (general acid catalysis) or with hydroxonium ions (specific acid catalysis). It is suggested that this entails the transfer of a proton to the substrate molecule with formation of positively charged protonated forms which exhibit an increased reactivity:

$$\begin{aligned} &AH + B \rightarrow BH^+ + A^- \text{ (general acid catalysis),} \\ &H_3O^+ + B \rightarrow BH^+ + H_2O \text{ (specific acid catalysis).} \end{aligned} \quad (1)$$

Their secondary reactions followed by decomposition lead to the regeneration of the catalyst and the formation of the final product. Here it is postulated that the protonated intermediate species have specific chemical properties which determine the selectivity of the acid catalysis. For example, it has come to be assumed that the acid-catalytic reactions of hydrocarbons are based on chemical reactions of the carbenium ions formed on proton transfer. On the other hand, the intermediate formation by secondary reactions of alkoxonium ions, etc. is characteristic of the reactions of alcohols.

If it is assumed, after Brønsted, that the proton transfer stage is rate-limiting, then the familiar correlation, which has come to be known as the Brønsted relation, should hold between the rate constants for the acid-catalytic reactions and the strength of the acids used as catalysts:

$$k = aK^{\alpha}, \quad 0 < \alpha < 1 \quad (2a)$$

or in the logarithmic form

$$\lg k = \alpha \lg K + C. \quad (2b)$$

These equations follow from the analogy between the proton transfer to water molecules, which is characterised by the acid dissociation constant K, and the proton transfer to the substrate molecules.

Eqns.(2) have been tested by Brønsted and his school for various acid-catalytic reactions, for example, for the decomposition of diazocompounds, the hydrolysis of esters, the enolisation of ketones, etc.[5] It was shown, within the limits of chemically similar groups of substances and acids, that the corresponding linear correlations do indeed hold between the logarithms of the equilibrium constants and the reaction rates, the proportionality coefficients C and α varying somewhat on passing from one group of substances to another. On the other hand, when the acid strength is varied within very wide limits, appreciable deviations from Eqns.(2) are usually observed. It must also be emphasised that Brønsted's reasoning is not sufficiently rigorous, because the analogy between the proton transfer to water molecules and the corresponding transfer to substrate molecules actually leads to a linear relation between the logarithms of the corresponding equilibrium constants, and not between the equilibrium acid dissociation constants themselves, and the rate constant for the proton transfer to a substrate molecule. In other words, Eqns.(2) presuppose the existence of a linear relation between the equilibrium constants and the rate of formation of the protonated form of the substrate.

Frequent attempts have been made to justify theoretically the existence of such a relation. Among them, the familiar model of intersecting unperturbed potential curves for the protonated states of the acid and substrate, proposed by Horiuti and Polanyi, merits most attention, its development having led subsequently to the creation of the theory of absolute reaction rates.[3,4] This model is not, however, confirmed by modern spectroscopic data, from which it follows that, for a sufficiently strong interaction beween an acid and a base, the form of the potential energy curve for proton vibrations is significantly perturbed (see Section III, subsection 4). Thus the Brønsted equation must be regarded as an empirical relation applicable to fairly narrow groups of substances and reactions rather than a rigorously theoretically justified relation.

2. Modern Ideas about the State of the Proton in Aqueous Solution

It is generally accepted that electrolytic dissociation in aqueous solutions is possible only as a result of solvation effects. Its contribution to the overall process energetics is decisive. For example, the heterolytic dissociation of the water molecule in the gas phase into the H^+ and OH^- ions is associated with an enormous energy expenditure, which is approximately 17 eV (1630 kJ mol^{-1}). However, in the liquid phase this energy is almost completely compensated by the sum of the hydration energies of the proton and the hydroxide ion. The endothermicity of the heterolytic dissociation of liquid water is therefore characterised by only 0.6 eV (or 60 kJ mol^{-1}), while the dissociation constant of this reaction is 1.8×10^{-16} g-ion litre^{-1}.

We shall consider the make up of the heat of hydration of the proton in liquid water. The affinity of the proton for the first water molecule is 7.4 eV ($\sim$710 kJ mol^{-1}). When the second and subsequent water molecules are added, the solvation energy decreases monotonically in the following sequence (the corresponding heats of hydration are given in brackets):

$$\begin{aligned} &H_3O^+ + H_2O \rightarrow H_5O_2^+ \quad (134 \text{ kJ mol}^{-1}), \\ &H_5O_2^+ + H_2O \rightarrow H_7O_3^+ \quad (96 \text{ kJ mol}^{-1}), \\ &H_7O_3^+ + H_2O \rightarrow H_9O_4^+ \quad (72 \text{ kJ mol}^{-1}), \\ &H_9O_4^+ + nH_2O \rightarrow H_9O_4^+ \cdot nH_2O \quad (79 \text{ kJ mol}^{-1}). \end{aligned} \quad (3)$$

Thus the overall proton hydration energy is 1100 kJ mol^{-1}. On the other hand, the heat of hydration of the hydroxide ion is smaller by approximately a factor of 2 and amounts to $\sim$500 kJ mol^{-1}.[5]

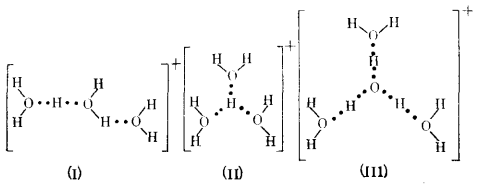
The exceptionally fine energy balance between the electrolytic dissociation processes in liquid water must be specially emphasised. The corresponding heat change represents the difference between two very large quantities—the energy of the heterolytic dissociation of the OH bond and the sum of the heats of solvation of the proton and the acid residues formed in this process. Although each of these quantities is approximately 1600 kJ mol^{-1}, the dissociation process is almost thermally neutral overall. Therefore, even very

slight changes in the energy of the abstraction of a proton from the acid molecule or in the heat of hydration of the proton in the acid residue have a marked influence on the character of the electrolytic dissociation. We shall return to this question below in the discussion of proton transfer to molecules with different basic properties in heterogeneous systems.

The main information about the real structure and geometry of the different hydrated forms of the proton in liquid water has been obtained from IR spectroscopic data, on the basis of quantum-chemical calculations, and with the aid of the results of other physicochemical measurements. Such information reduces to the following findings.[5]

The simplest stable state of the hydrated proton in liquid water is the hydroxonium ion H_3O^+ and the symmetrical very slightly polarised ion $O_2H_5^+$.[6-8] Regardless of the nature of the initial acid, it is characterised by a continuous absorption in the IR in the range $1000-3500$ cm^{-1}. In this structure the proton is not localised in the vicinity of one of the oxygen atoms but oscillates between them; this agrees with the estimated average lifetime of the H_3O^+ ion in liquid water (2×10^{-13} s).[5] For a theoretical interpretation of the continuous absorption, two approaches have been suggested: in one of them account is taken of the inter-relation between the proton transitions and the phonon spectrum of the medium,[9] while in the other account is taken of the inter-relation between the proton transitions and the vibrations of the hydrogen bond.[10,11] In both cases, a satisfactory agreement with experiment is achieved.

Of the two versions of the addition of yet another water molecule to the $O_2H_5^+$ ion that which leads to the linear structure (I) is preferred, because the structure (II), which has C_{3v} symmetry and the trigonal configuration, is less stable owing to the strong electrostatic repulsion between the negatively charged oxygen atoms.



(I) (II) (III)

The linear structure (I) is also very slightly polarised, because even the smallest distortion of the geometry leads to the localisation of a proton on the right- or left-hand side of the chain of water molecules.

As can be seen from Eqns.(3), further hydration of the $O_3H_7^+$ ion also produces a considerable energy gain, which agrees with the finding that the most stable structure and therefore the structure which predominates in aqueous solutions is the symmetrical trigonal $O_4H_9^+$ (III). It can be assumed that the proton in the structure (II) oscillates continuously between two neighbouring oxygen atoms, i.e. it forms part of the composition of the continuously migrating simplest species $O_2H_5^+$. The ease of its formation and decomposition in the oscillations of the water molecules linked by hydrogen bond network does explain the high mobility of the proton in aqueous solutions. In other words, the familiar Grotthus relay mechanism of proton migration in liquid water is a consequence of the high polarisability of the simplest solvated $O_2H_5^+$ fragments.

3. Proton Transfer in Non-aqueous Media

Certain details of the mechanism of proton transfer from acid molecules to solvent or substrate molecules can be more readily traced in non-aqueous solutions, since the IR spectra do not then show the broad lines due to the hydroxy-groups linked by the hydrogen bond network. This makes it possible to investigate the influence of the successive addition of several molecules on the protonation. Such measurements by IR spectroscopy have been carried out recently by ourselves for the interaction of HCl and HBr with the molecules of water, methyl, ethyl, and isopropyl alcohols, and diethyl ether in CCl_4, CH_2Cl_2, and nitromethane.[12,13] The dilute solutions used in these studies contained an acid ($0.02-0.2$ M) and the substrate ($0.01-0.5$ M).

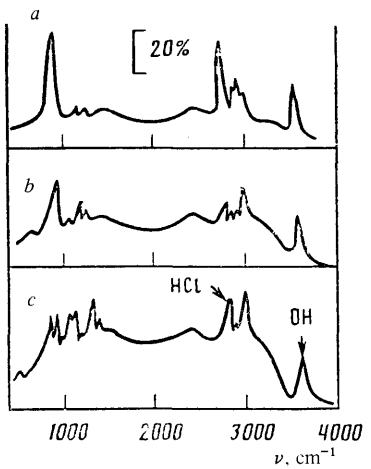
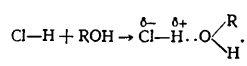


Figure 1. IR absorption spectra of the complexes of methyl alcohol (a), ethyl alcohol (b), and isopropyl alcohol (c) with HCl in CCl_4. Alcohol concentration 5×10^{-2} M; acid concentration 3×10^{-2} to 6×10^{-2} M.[12]

Fig.1 presents typical IR spectra of the complexes of HCl with methyl, ethyl, and isopropyl alcohols in CCl_4. Narrow lines due to the stretching vibrations of the H—Cl, C—H, and O—H bonds are observed against the background of the broad bands due to the HCl molecules perturbed by a hydrogen bond. In addition there is also a continuous absorption analogous to that observed previously for $O_2H_5^+$ ions in aqueous solutions,[6,7] i.e. the absorption induced by the oscillations of protons between two oxygen atoms. The measurements carried out for different ratios of the acid and alcohols showed that the intensity of the broad lines near 2400 cm^{-1}, due to the presence of HCl molecules perturbed by the hydrogen bond, increases linearly with increasing alcohol concentration. On the other hand, the narrow line associated with the free HCl molecules at 2820 cm^{-1} diminishes linearly. This result was explained by the

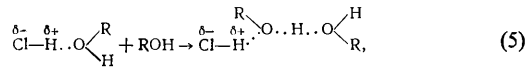
formation of 1 : 1 complexes between acid and alcohol molecules via a strong hydrogen bond:



(4)

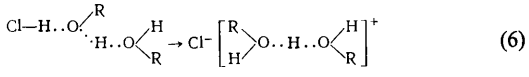
In contrast to this, the intensity of the continuous absorption, measured at 2000 cm^{-1}, increased in proportion to the square of the concentration of the alcohol or water molecules, which made it possible to attribute the composition HCl.2ROH to the alcohol complexes. Apparently, even in the case of a strong acid such as HCl, complete proton transfer occurs immediately to only two alcohol molecules. This entails the formation of complexes, resembling the $O_2H_5^+$ ions in aqueous solutions, in which the proton oscillates between two oxygen atoms. This in fact leads to the appearance of the analogous continuous absorption in the IR spectrum. On the other hand, the proton affinity of one alcohol molecule is sufficient only for the formation of complexes with a strong hydrogen bond.

The mechanism of proton transfer to two alcohol molecules may be analogous to the mechanism of the relay transfer in liquid water. Yet another hydrogen bond is formed initially with participation of a second alcohol molecule:



(5)

and this is followed by the vibrational excitation of such an associated species, which leads to complete proton transfer:



(6)

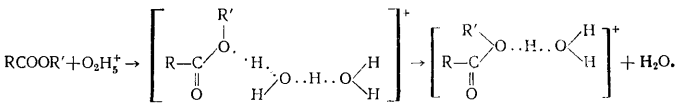
The proton is also apparently transferred via the same mechanism to two water molecules, while the interaction with one water molecule also results in the formation of a complex with only a moderately strong hydrogen bond. The HCl stretching vibration band then shifts from 2820 and 2500 cm^{-1}. We may also note that the shifts of the vibration frequency of the hydrogen bond-perturbed acid molecules in the 1 : 1 complexes and the intensity of the continuous absorption of the 1 : 2 complexes agree well with the substrate basicity series (H_2O < CH_3OH < C_2H_5OH < C_3H_7OH) and the acid strength series (HBr > HCl). In the case of aqueous solutions, the conclusion that a proton is transferred to two water molecules at once was reached also in relation to films of polyfluorosulphonic acid[6] and sulphuric acid solutions.[14,15]

The proton transfer in non-polar solvents from a wide range of weak and strong acids to the molecule of a strong base (pyridine) has been investigated.[16] The protonated forms were detected only after the interaction with very strong acids (HNO_3, HCl, HBr, $HClO_4$). Weaker acids form only hydrogen-bonded complexes whose stability varies within wide limits. These data also evidently indicate only a weak tendency towards proton transfer only in non-polar solvents. The reduced tendency towards proton transfer and the absence of solvation effects have likewise been observed in the gas phase[17] and in inert gas matrices.[18]

4. Modern Ideas about the Mechanism of Homogeneous Acid Catalysis

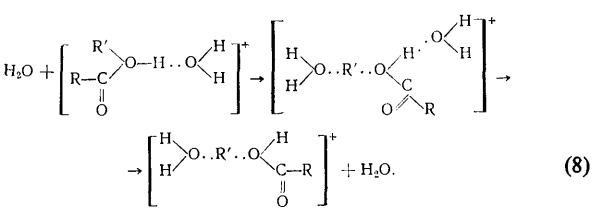
The results described above indicate a decisive role for the interaction of the acid with several water or substrate molecules in the transfer of a proton to the latter. Therefore, in discussing the mechanism of homogeneous acid catalysis in aqueous solutions, it is evidently insufficient to consider only the interaction of the reacting molecules with hydroxonium ions or with undissociated acid molecules alone and account must be taken also of the possibility of the formation of more complex solvated complexes including several water molecules. This conclusion agrees with the results obtained in a study of the kinetics of the hydrolysis of esters in aqueous solutions of strong acids:[14,15] it was shown that the activated complex involves the $O_2H_5^+$ ion and not the hydroxonium ion H_3O^+. We shall consider the possible mechanism of this reaction in greater detail.

It appears likely that its first stage is proton transfer from the $O_2H_5^+$ ion to the ester molecule, which is analogous to the proton transfer via a chain of hydrogen-bonded water molecules:



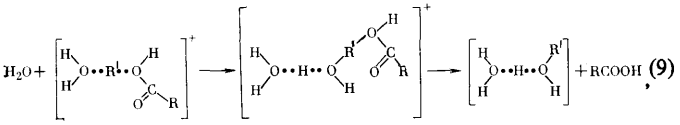
(7)

The positively charged ion of the protonated ester is then solvated by yet another water molecule, which results in the localisation of the positive charge on the R′ fragment:

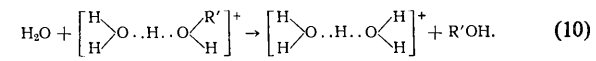


(8)

The decomposition of this complex (also with participation of a water molecule) then leads to the formation of an acid and the protonated alcohol, which loses its proton as a result of yet another reaction involving a water molecule:



(9)



(10)

Thus water participates in all the intermediate stages of the catalytic reaction. Its driving force is the high polarisability of the complexes incorporating a solvated proton, which are readily formed and decomposed under the influence of the vibrations of the solvent molecules surrounding them. This entails a "switchover", as it were, from the dissociating bonds to the newly formed bonds induced by the proton migration along the hydrogen-bonded chain of molecules.

This mechanism differs from that considered in the literature,[14,15] but we believe that it agrees better with modern data concerning the state of the hydrated proton in aqueous solutions and concerning the mechanism of proton transfer in liquid water. It also confirms the idea of "bond redistribution chains" developed for enzyme catalysis[19,20] and the mechanisms of proton transfer in biological systems discussed in a number of studies.[21–23]

III. HETEROGENEOUS ACID CATALYSIS

The ideas about the mechanisms of heteogeneous-catalytic reactions of hydrocarbons were formulated much later than for the the homogeneous acid catalysis—not until the end of the 1940's and the beginning of the 1950's. At that time, a number of workers put forward independently the hypothesis of the carbenium ion mechanism of the reactions in question[24–28] based on purely chemical analogies with low-temperature reactions of hydrocarbons in the presence of strong acids (the higher reactivity of olefins compared with paraffins, the high reactivity of compounds with a tertiary carbon atom, the selective formation of isoparaffins under the catalytic conditions, the occurrence of olefin isomerisation, hydrogen transfer, and hydrogen isotope exchange reactions, etc.).

The next important step was the experimental demonstration of the acidity of amorphous aluminosilicates and certain other oxide catalysts based on the use of the absorption of ammonia and Hammett indicators.[29,30] These studies led to the widespread adoption of the idea that adsorbed carbenium ions exist on the surfaces of oxide catalysts and that they play a decisive role in the mechanisms of the catalytic reactions of hydrocarbons, although this hypothesis was never in fact subsequently confirmed by direct spectroscopic methods.

Multistage schemes, analogous to those for general acid catalysis in solutions, are usually postulated for the mechanisms of heterogeneous-catalytic reactions of hydrocarbons.[31–34] For example, for the catalytic reactions of olefins, it is suggested that the adsorbed molecules are initially linked by strong hydrogen bonds to the acid hydroxyls. Complete proton transfer then takes place with formation of adsorbed carbenium ions. It is also assumed that such protonated intermediate forms exhibit an enhanced specific reactivity, which explains the selectivity of the corresponding heterogeneous-catalytic reactions. For example, the reverse abstraction of a proton from them leads to the migration of the double bond in the olefin molecules. Linear carbenium ions can isomerise to branched ions, which induces the skeletal isomerisation of the hydrocarbons. The occurrence of cracking, etc. is explained by the splitting off of carbenium ions from olefin molecules. In particular, the fairly typical mechanism of the heterogeneous-catalytic reactions of but-1-ene can be represented as follows in accordance with these ideas:

$$\begin{aligned} &CH_2{=}CH{-}CH_2{-}CH_3 + H^+ \rightarrow CH_3{-}\overset{+}{C}H{-}CH_2{-}CH_3 \rightarrow \\ &\rightarrow CH_3{-}CH{=}CH{-}CH_3 + H^+ \text{ (migration of the double bond)}, \\ &\rightarrow CH_3{-}\overset{CH_3}{\overset{|}{\underset{+}{C}}}{-}CH_3 \rightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3 + H^+ \text{ (skeletal isomerisation)}, \\ &\rightarrow CH_2{=}CH_2 + C_2H_5^+ \rightarrow 2C_2H_4 + H^+ \text{ (cracking)}. \end{aligned} \qquad (11)$$

Although such schemes have come to be widely adopted in the literature and they describe satisfactorily the composition of the products of heterogeneous-catalytic reactions of hydrocarbons, from our point of view they are no longer consistent with the significance which is nowadays attributed to the concepts of the mechanism of catalytic reactions. Indeed, carbenium ions are not in fact free but are adsorbed on the catalyst surfaces. Therefore, depending on the strength of the acid centres or on the nature of the basic centres to which the carbenium ions are bound during adsorption, their chemical properties can vary within extremely wide limits. For example, it is known that the migration of the double bond in olefins takes place on weaker acid centres than their skeletal isomerisation.[34] This difference is not, however, taken into account by Scheme (11). It also fails to reveal the driving forces of various elementary reactions on the adsorbed carbenium ions. Furthermore, these processes have come to be part of the order of the day by virtue of the results obtained in the study of proton transfer by modern spectroscopic methods and the results of quantum-chemical calculations. Their discussion is the main aim of the present article.

1. Spectroscopic Data on the Protic Acid Centres on the Surfaces of Oxide Catalysts

Among acid catalysts, amorphous and crystalline aluminosilicates (zeolites), alumina, aluminium phosphate, phosphoric acid on silica gel, etc. have come to be most widely used. Their active centres are acid hydroxy-groups, which are formed on the surfaces of the oxides on partial hydrolysis of the metal–oxygen bonds (the so called terminal OH groups) or when the protons compensate the excess local negative charge on the surface fragments (the so called structural OH groups). The number of these groups, determined from the intensity of the proton resonance spectra or by the method involving isotope exchange with molecular deuterium, usually corresponds to only a few per cent of the monolayer coverage. If such hydroxy-groups have fairly pronounced acid properties, then they do play the role of the active centres in heterogeneous acid catalysis.

Brønsted centres of both types have been studied in detail by IR spectroscopy[35,36] and NMR,[37,38] which made it possible to obtain detailed information about their geometry, the energy barriers to the rotation of the $M\diagup^{O}\diagdown H$ fragment, and certain other parameters characterising such centres. In particular, it has been demonstrated by IR spectroscopy that the number of different hydroxy-groups on the zinc oxide surface is three, while on the surface of nickel(II) oxide it is four. There are OH groups of five different types on the surface of alumina. The discrete character of the distribution of the hydroxy-groups is characteristic also of the hydrogen-forms of the zeolites.

A systematic treatment has been proposed[39,40] for the surface hydroxy-groups based on the hypothesis that the frequency of their stretching vibrations depends primarily on the coordination number of the oxygen atoms in relation to the surrounding cations. In other words, it was assumed that the nature of the OH bond is determined mainly by the character of the hybridisation of the orbitals of the oxygen atom. On the other hand, there exists the view that the stretching vibration frequency of the hydroxy-groups depends predominantly on the acid–base properties.[41] This is based on the fact that stretching vibration frequencies of 3839 and 2955 cm^{-1} are characteristic of the free OH^- ion and the OH^+ ion respectively.[42] Thus the lower-frequency hydroxy-groups have acid properties and the higher-frequency groups have basic properties.

However, the stretching vibration frequency of the hydroxy-groups can also be influenced by a number of other factors. It is therefore extremely desirable to measure not only the fundamental frequency

of the stretching vibrations of the OH bond but also other parameters characterising it.

This can be done with the aid of the diffuse scattering IR spectroscopy, the great possibilities of which have been demonstrated in a number of studies.[43-49] This method makes it possible to extend greatly the range of spectroscopic measurements, including the frequencies of the first and second overtones of the stretching vibrations of the surface OH groups, and to calculate from these data the energies of their homolytic dissociation and the parameters of the Morse functions ω_e and x for the OH bond. The results obtained indicate that the vibrations of the OH groups, which virtually do not interact with the vibrations of the oxide lattices, are highly characteristic. It was also found that the frequencies of the deformation vibrations of the surface hydroxy-groups contain most information as regards the nature and geometry of such groups. They are difficult to measure directly owing to the marked absorption of light by the oxide lattice in the range $800-1500$ cm^{-1}, but it is possible to obtain them as differences between the frequencies of the combination stretching-deformation vibrations and the frequencies of the stretching vibrations. The lowest deformation vibration frequency ($\sim 700-800$ cm^{-1}) is that of terminal OH groups. On passing to bridging hydroxy-groups, whose oxygen is linked to two cations of the oxide lattice, the deformation vibration frequency increases to $1000-1100$ cm^{-1}. This can be explained by the increase in the rigidity of the M⟨OH⟩M fragment when oxygen is coordinated to the second cation. For hydroxy-groups with a still higher oxygen coordination number, the combination stretching plus deformation vibrations frequencies are usually not observed at all, so that the number of bands in the fundamental region of their IR spectrum is greater than in the combination region. The results of these measurements make it possible to refine and test the conclusions concerning the nature and geometry of the surface hydroxy-groups reached from the analysis of the fundamental stretching vibrations frequencies alone.

IR spectroscopy is used widely also in quantitative measurements of the acid strength of the surface hydroxy-groups. The bathochromic shifts of the stretching vibration frequencies, induced by the formation of hydrogen bonds with the molecules of different bases, are usually employed for this purpose. These shifts are linearly correlated both the with acidity of the OH groups and with the basicity of the molecules interacting with them:[50,51]

$$\Delta\nu_{OH}/\nu_{OH} = a - b\Delta pK_a, \qquad (12)$$

where $\Delta pK_a = pK_a^{ac} - pK_a^{bas}$, ν_{OH} and $\Delta\nu_{OH}$ are the stretching vibration frequency of the OH group and its shifts induced by interaction with the molecules of bases, pK_a^{ac} is the logarithm of the acid dissociation constant, and pK_a^{bas} the logarithms of the basicity constants of the corresponding bases.

Thus pK_a^{ac} for the OH surface groups on any one oxide can be determined from a series of shifts induced by the adsorption on it of several weak bases characterised by different pK_a^{bas} values. On the other hand, the frequency shifts, induced by the adsorption of the same base, for example, benzene or carbon monoxide, on the surfaces of different oxides, are usually measured to compare the acidities of their hydroxy-groups. Studies involving the use of IR spectroscopy of the acid–base properties of oxides have been surveyed in a review.[52]

2. Quantum-chemical Cluster Models of the Surface Hydroxy-groups and the Nature of Their Acidity

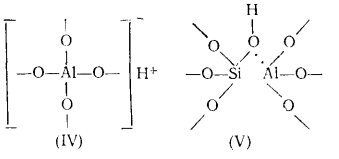
The nature of the acidity of the OH groups can also be analysed with the aid of quantum-chemical calculations performed using the so called "cluster" models.[53-58] The simplest model of an OH acid is the A–O–H molecule, where A is a hydrogen-like atom, whose ionisation potential can be varied within wide limits. If it is equal to 13.6 eV, as for the hydrogen atom, then a structure of this kind models the neutral water molecule. Lower ionisation potentials correspond to alkali metals, whereupon the hydroxy-groups are negatively charged and acquire basic properties. On the other hand, higher ionisation potentials correspond to ions with a high positive charge such as N^{5+}, P^{5+}, S^{6+}, etc. The electron density then shifts to the A atom, imparting acid properties to the hydroxy-groups.

These effects can be described more rigorously using clusters taking into account the real structure of the oxide surfaces. For example, in the case of terminal hydroxy-groups on the silica surface, one frequently considers the $Si(OH)_4$ or $SiOH(OA)_3$ clusters, where A are hydrogen-like atoms, as for the simplest clusters.

It follows from the foregoing that one of the causes of the formation of strongly acid terminal hydroxy-groups on the oxide surfaces is the polarising effect of neighbouring highly charged cations. Accordingly, the surfaces of partly hydrolysed alkali and alkaline earth metal oxides have basic properties, while the terminal groups on the TiO_2, V_2O_5, and MoO_3, or WO_3 surfaces have acid properties. The strength of the centres then increases with increasing positive charge on the cations. With the exception of WO_3, these oxides are not, however, used in heterogeneous acid catalysis because, at a high temperature in the presence of hydrocarbons or other reductants they readily pass to lower valence states.

Mixed oxides, among which crystalline skeletal aluminosilicates (zeolites) and amorphous aluminosilicates are most important, are much more significant for acid catalysis. They are characterised by the presence of structural bridging hydroxo-groups in which the coordination number of oxygen in relation to the cations is two.

The crystal lattice of aluminosilicates is constructed of oxygen tetrahedra at the centres of which are silicon or aluminium atoms. When it is described in terms of the ionic model, the aluminium-occupied tetrahedra carry a single excess negative charge, which is compensated by the charges of the adjoining cations or protons with which the Brønsted acidity of the aluminosilicates [structure (IV)] is in fact associated:



Within the framework of the covalent model (V), the acid centre may consist of a terminal silanol group, whose oxygen is linked by a coordinate bond to an adjoining aluminium atom (a Lewis acid centre). The combination of the Brønsted and Lewis acid centres shifts the electron density from oxygen to aluminium, diminishes the negative charge on the OH group, and enhances its acid properties.

In amorphous aluminosilicates, the number of such bridging acid groups is small and only a small proportion of the entire aluminium content corresponds to them. On the other hand, the vast majority

of the hydroxy-groups formed on hydrolysis of the surfaces are terminal OH groups with weakly acid properties.[36]

The situation is different in the hydrogen-forms of zeolites—aluminosilicates with a strictly regular crystal structure. Ideally the number of acid hydroxy-groups is in this instance identical with the number of aluminium atoms present in the lattice, i.e. it is many times greater than in amorphous aluminosilicates. This in fact explains the high catalytic activity of zeolites.[59,60]

Quantum-chemical cluster models of hydroxy-groups in zeolites have been developed,[61] and the calculations performed have shown that, with increase in the number of neighbouring aluminium atoms, the acidity of the hydroxy-groups diminishes monotonically; this can be inferred from the decrease in the positive charge on the proton and from the increase in the energy of its abstraction from the corresponding clusters. It has also been concluded that a characteristic feature of crystalline aluminosilicates with a definite silicon : aluminium ratio is the presence of hydroxy-groups with a constant number of nearest aluminium atoms. For example, in high-silica zeolites, the bridging hydroxy-groups are surrounded solely by silicon atoms. They are therefore characterised by identical Brønsted acid centres of identical strength.[62] With increase in the number of aluminium atoms in the crystal lattice, for example in the case of faujasites, hydroxy-groups having two or three neighbouring aluminium atoms appear and the character of the Brønsted acidity changes, which has in fact been confirmed experimentally.[34]

Thus quantum-chemical cluster models permit an atomic-molecular description of the structure of the acid centres in zeolites and explains satisfactorily the discrete character of the variation of the acidity in specimens with different aluminium contents in the lattice.[63,64] It is no less significant also that, with their aid, one can carry out fairly well-founded quantitative calculations of the intermediate structures in heterogeneous acid-catalytic reactions, which will be discussed below.

Analogous atomic-molecular models have also been used to treat systematically the hydroxy-groups on the surfaces of other oxides, for example, alumina.[41] There is no doubt that in the future this approach will permit a rational systematic treatment of the surface OH groups on oxides with a wide variety of different acid–base properties.

3. The Nature of the Protonated Intermediate States on the Surfaces of Oxide Catalysts

As already stated above, heterolytic dissociation in solution is possible only in the presence of solvation effects, whose contribution to the process energetics is decisive. Therefore proton transfer on the surfaces of heterogeneous oxide catalysts during high-temperature gas-phase reactions in the absence of polar solvents differs radically from the protonation in aqueous solutions.

Under the conditions of heterogeneous acid catalysis, the situation approaches more closely to the proton transfer in non-polar solvents discussed above where the solvation effects are minimal and the protonation of the substrate is associated with additional energy expenditure. For the majority of adsorbed molecules, the proton transfer is therefore significantly endothermic. It becomes energetically favourable in the interaction of very acid hydroxy-groups with strong bases such as ammonia, pyridine etc. These molecules are in fact usually employed as indicators for strongly acid surface OH groups. However, in this connection the fact has been overlooked that, even if adsorbed ammonium or pyridinium ions are actually formed from them on the surfaces of acid type catalysts, this by no means implies that analogous ionic intermediate compounds arise also in the adsorption of olefins or even paraffins, whose proton affinity is much smaller than those of ammonia or pyridine. In fact, in the interaction of hydrocarbons even with very strongly acid Brønsted centres, either complexes with a short hydrogen bond or highly polarised covalent structures are produced. Thus the intermediate active forms in heterogeneous acid catalysis differ significantly from the protonated ionic states in aqueous solutions and other polar sovlents and resemble more closely the complexes formed in the interaction of strong acids with weak bases or of weak acids with strong bases in non-polar solvents.

In this connection, it is appropriate to recall that the concept of carbonium ion mechanisms arose in organic chemistry exclusively on the basis of indirect kinetic and stereochemical data and also as a result of studies on the final products of the corresponding reactions. Carbonium ions are then regarded as short-lived species which cannot be observed directly by physical methods.[65] On the other hand, in heterogeneous catalysis the formation of adsorbed carbonium or carbenium ions is frequently understood too literally, as the solid catalysts are not superacids and solvation effects, stabilising the intermediate structures, are absent in the catalytic reactions of hydrocarbons.

Indeed, surface esters and not ion pairs are formed in the interaction of Brønsted acid centres with olefins or alcohols. These are known to be covalent compounds, as is confirmed by their dipole moments and by the comparatively small low-field chemical shifts in the ^{13}C NMR spectra involving the α-carbon atoms of the alkyl substituents, which do not differ from the chemical shifts in the corresponding alcohols and are in the range 50–70 p.p.m.[66] On the other hand, the shifts for stable carbenium ions in superacid solutions, where the positive charge on the carbon is much higher, reach 300–350 p.p.m. For example, the chemical shift for the central atom in the $(CH_3)_3C^+$ is 335.7 p.p.m. and that for the carbon atom in the $(C_2H_5)_3C^+$ ion is 331.8 p.p.m.[70]

The covalent nature of the C–O bond in the surface esters has also been confirmed by quantum-chemical calculations. Thus it has been shown[67] that the interaction of ethylene with the bridging hydroxy-group of a high-silica zeolite leads to the formation of a surface ethoxy-fragment carrying a comparatively low positive charge of +0.26 e, and not a carbenium ion, while the interaction of an ammonia molecule with the same hydroxy-group results in the formation of an ammonium ion, whose charge is +0.71 e.[68] On the other hand, it follows from quantum-chemical calculations that the tendency towards an increase in the amount of ionic character of the C–O bond in esters increases with increase in its length or on vibrational excitiation.[69] Thus the carbenium ion properties of the alkyl substituents are manifested not in the ground states of the corresponding intermediates but in their transition stages.

The complete rejection of the mechanisms involving adsorbed carbenium ions, which are nowadays generally accepted, does not by any means follow from the foregoing. We merely wish to emphasise yet again that the concept of carbenium ions refers more to transition states than to intermediate compounds. On the other hand the very concept of the "adsorbed carbenium ion" may have a completely different significance in each specific case. From our point of view, it should be understood not as the real existence of contact ion pairs on the surfaces of catalysts but rather as implying the presence of intermediate compounds resembling carbenium ions in the liquid phase as regards their reactivity.

4. Spectroscopic Studies on the Elementary Proton Transfer Stage on the Surfaces of Oxide Catalysts

The reduced tendency towards the formation of ionic structures in the proton transfer from acid hydroxy-groups to molecules adsorbed on the surfaces of heterogeneous catalysts has been confirmed also by spectroscopic data. Above it was already stated that the bathochromic shifts of the stretching vibrations of the OH groups, induced by the formation of a hydrogen bond with the adsorbed molecules, are widely used for the measurement of the strength of the Brønsted acid centres on the surfaces of oxides. The possibilities of IR spectroscopy in the study of the proton transfer mechanism are not, however, exhausted by this. It has been suggested[43,48,71–75] that, together with the shifts of the fundamental stretching vibration frequency, one should also measure the bathochromic shifts of the overtones of the stretching vibrations. These data make it possible to reconstruct the lowest sections of the potential curves for the OH bond in the surface complexes preceding the proton transfer and to calculate the height of the potential barrier in this elementary stage.

Indeed it is well known that the potential energy curve for a diatomic molecule can be constructed from the positions of any two of its vibrational levels. It has been shown[43,44] that, as a consequence of the characteristic nature of the stretching vibrations, the surface OH groups can also be regarded as diatomic fragments which hardly interact with the lattice vibrations of the oxide. Therefore the lowest sections of the potential curves for the OH bond in the free hydroxy-groups and in the hydrogen-bonded complexes can be plotted from the fundamental frequencies and overtones of the OH group vibrations. On the other hand, for the reconstruction of the complete potential energy profile of the elementary proton transfer stage, one can assume to a first approximation that the stage corresponds to an increase in the length of the OH bond by approximately 0.05 nm, which follows from the considerations described above.

It is known that the lengths of the strong hydrogen bonds in a wide variety of complexes are in the range 0.24–0.26 nm.[76] On the other hand, the equilibrium O–H distance in the initial hydroxy-groups is approximately 0.1 nm. Similar values are characteristic also of the length of the C–H (0.109 nm), N–H (0.101 nm), and other bonds formed in protonated intermediate compounds. The extension of the O–H bond by approximately 0.05 nm therefore corresponds to proton transfer to adsorbed molecules and a somewhat smaller increase in its length corresponds to the apex of the potential proton transfer barrier. As regards the complete potential energy profile for the elementary proton transfer stage, the latter can be obtained by positioning the potential curve for the OH bond, calculated from spectroscopic data, and the potential curve for the bond newly formed in the protonated compound in such a way that the distance between their minima is 0.05 nm.

Fig.2 presents the potential energy profiles constructed in this way for the exothermic and endothermic proton transfer stages.[73–75] In the former case, the transfer requires virtually no activation energy. On the other hand, for the endothermic stages the formation of the stable intermediate protonated compounds is possible only provided that the energy expenditure on the proton transfer does not exceed approximately 100 kJ mol^{-1}. Otherwise, the local minimum on the potential curve corresponding to the formation of the protonated state is either absent or its depth is so small that the protonated state is metastable and decomposes even after a few vibrations. This is caused by the comparatively large width of the lowest section of the potential curve for the OH bond and the slight increase in its length on complete proton transfer in its surface complexes. In this respect, heterogeneous acid catalysis differs significantly from homogeneous acid catalysis in aqueous solutions, where the proton transfer reaction coordinate does not have the significance of a simple increase in the length of the OH bond and is accompanied by a rearrangement of many solvent molecules, resulting in the separation of cations and anions in space. Therefore, in aqueous solutions protonated states can really exist even if proton transfer is significantly endothermic.

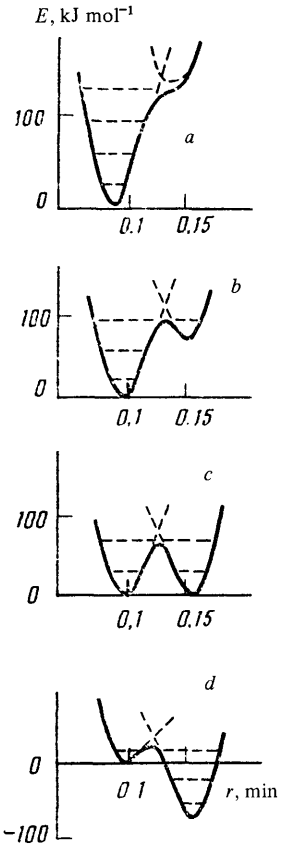


Figure 2. The potential energy profiles for the elementary proton transfer stage constructed on the basis of spectroscopic data:[73,74] (a) process endothermicity 150 kJ mol^{-1}; (b) process endothermicity 100 kJ mol^{-1}; (c) thermally neutral process; (d) process exothermicity 50 kJ mol^{-1}.

It is possible to formulate several spectroscopic criteria for the determination of the real tendency towards proton transfer to the adsorbed molecules. The most clear-cut of these is the increase in the anharmonicity of the potential curve for the OH bond on formation of surface complexes. To use a picturesque phase, the anharmonicity makes it possible to analyse the response of the acid hydroxy-group to the extension of the OH bond and to the

approach of the adsorbed molecule by the proton. The increase in anharmonicity indicates the attraction of the proton to the substrate and its decrease indicates the repulsion.[77]

The isotope effect, i.e. the ratio of the vibration frequencies of the light and heavy hydroxy-groups perturbed by hydrogen bond formation, may be used as another criterion of the positive tendency towards the formation of protonated states (the ratio diminishes with increase in anharmonicity and in positive tendency towards proton transfer). Furthermore, the tendency towards proton transfer is manifested by the absence of strong perturbation of the first overtone and in the large bathochromic shifts of the stretching vibrations in the spectra of hydrogen-bonded complexes (400–600 cm^{-1} and above).

The application of these criteria to the analysis of the IR spectra of the complexes of hydroxy-groups with various molecules also indicates merely a moderate tendency towards the formation of ionic intermediate structures under the conditions of heterogeneous catalysis. For example, in the benzene complexes with acid hydroxy-groups of the hydrogen-form of the type Y zeolite, the decrease in the fundamental stretching vibration frequency is approximately 350 cm^{-1}. This, however, is insufficient for the complete proton transfer to benzene molecules. The anharmonicity coefficient also increases only up to 4×10^{-2}, i.e. by a factor of approximately two. Approximately the same bathochromic shifts are observed likewise in the interaction of acid hydroxy-groups of the type HY zeolite with ethylene.[78]

The proton affinities of certain molecules.[80]

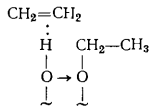
Molecule	Proton affinity, eV	Molecule	Proton affinity, eV
H_2	4,4	C_4H_8	7,8
CH_4	5,1	CH_3OH	7,8
C_2H_6	5,6	C_3H_8	7,9
C_3H_8	6,1	CH_3CHO	8,0
C_2H_4	6,9	CH_3CN	8,1
H_2O	7,1	C_2H_5OH	8,1–8,4
C_6H_6	7,5	CH_3OCH_3	8,5
cyclo-C_6H_{10}	7,7	NH_3	9
CH_3NO_2	7,7–7,8	CH_3NH_2	9,2

The formation of ion pairs hardly occurs even in the interaction of ethylene with the very highly acid hydroxy-groups of the high-silica zeolites of type ZSM-5. This is indicated both by the moderate shifts of the OH vibration frequencies in the spectra of the hydrogen-bonded complexes and by the linear structure of the ethylene oligomers formed at room temperature, which cannot be explained by steric effects, because the polymerisation of propene on the same catalysts leads to the formation of branched structures in their channels.[79] Apparently, in conformity with the quantum-chemical calculations already discussed above, the interaction of ethylene with such centres entails the formation of highly polarised covalent structures and not ion pairs. Thus spectroscopic data also demonstrate that the concept of carbenium ions is too simplified when applied to heterogeneous systems.

We may note that the transition from the hydrogen-bonded complexes to polarised covalent structures and further to surface contact ion pairs depends very markedly on the energetics of the elementary stage of proton transfer. For example, the benzene is not protonated in its interaction with the acid OH groups of a type Y zeolite (the proton affinity of benzene is 7.5 eV—see Table), but contact ion pairs are undoubtedly formed in the interaction of these groups with ammonia (the proton affinity is 9 eV [80]). Thus the proton transfer and the formation of contact ion pairs require an additional energy of only approximately 1.5 eV. There is nothing surprising in this, because a free energy change of 5.7 kJ mol^{-1} corresponds to one unit on the pK_a scale in aqueous solutions and a free energy change of approximately 120 kJ mol^{-1} or 1.2 eV corresponds to the transition from a weak acid with $pK_a = +10$ to superacids with $pK_a = -10$. Solvation in fact makes good this deficiency in the formation of intermediate ionic states and contributes to the energy balance of the acid–base interaction in aqueous solutions. On the other hand, in the high-temperature catalytic reactions of hydrocarbons, this source of additional energy is absent. It cannot be replaced by the activation energy either, because, as already mentioned above, in the case where the proton transfer stages are insufficiently endothermic minima corresponding to protonated ionic structures are missing from the potential energy surface.

5. The Reaction Coordinate in Heterogeneous Acid Catalysis. Synchronous Mechanisms of Acid Catalytic Reactions

In constructing the energy profiles, discussed in the previous Section, for the elementary proton transfer stage, no account is taken of the additional energy gain associated with the optimisation of the geometry of the protonated state. For example, the conversion of a π-complex of ethylene into the ethoxy-fragment actually involves, apart from the extension of the OH bond as the proton approaches the ethylene molecule, also an increase in the length of the C=C bond when it is converted into a single bond, a change in the hybridisation and in the valence angles in the CH_2 and CH_3 groups, and the orientation of the adsorbed molecule relative to the catalyst surface:



(13)

In other words, the vibrational excitation of the OH bond and the associated increase in length by no means always constitute the optimum coordinate of the elementary protonation stage.

Depending on the relative contributions of various factors, there is a possibility of a wide variety of situations in this instance. For example, the role of relaxation in the formation of the ammonium ion from adsorbed ammonia is minimal. On the other hand, in the example involving the formation of the ethoxy-fragment just discussed, the optimisation of the geometry is extremely significant and the reaction coordinate corresponds to only a very slight extent to an increase in the length of the OH bond. In similar cases we shall henceforth speak of a synchronous mechanism of heterogeneous catalytic reactions involving the simultaneous activation and rearrangement of many chemical bonds in the adsorbed molecules or intermediate complexes.

The advantage of these mechanisms under the conditions of acid–base homogeneous catalysis compared with the multistage consecutive protonation-deprotonation of the substrate molecules was noted as early as the end of the 1950's by Syrkin.[81–83] It was

concluded in this connection that there is a possibility of the formation of cyclic five-, six-, and seven-membered transition states and their role in hydrolytic, esterification, Friedel–Crafts, etc. reactions was discussed.[84–86] In relation to heterogeneous catalysis, the important role of synchronous or joint mechanisms in heterogeneous catalysis has been discussed by Boreskov mainly in relation to catalytic oxidation reactions.[87]

The pre-exponential factors in the rate constants for such complex elementary stages are naturally smaller than the stretching vibration frequency of the OH bond because a concerted change in a large number of different coordinates takes place at once in the transition state or many vibrations are found to be in phase. This more complex reaction pathway is associated, however, with a lower energy barrier to the formation of the intermediate protonated state. This more than makes up for the lower activation entropy for the protonation stage and ensures a high rate of the catalytic reaction.[88]

The limiting case in such synchronous mechanisms in acid catalysis involves reactions where the intermediate protonated forms are not formed at all. This is apparently typical of molecules with a low proton affinity, for example, for hydrogen or the paraffins. Since the formation of the intermediate protonated state is unfavourable in this instance, a new bond between the molecule or its fragment and the catalyst surface is formed simultaneously with proton transfer which apparently at least partly compensates for the energy of the abstraction of the proton from the acid centre. For example, in heteroisotope exchange reactions, the proton transfer to the acid centre of the substrate is accompanied by the simultaneous reverse reaction involving the abstraction of another proton from the activated complex. On the other hand, the energy involved in binding the second proton compensates for the difficulty of transferring the first proton to the substrate molecule analogously to the promotion of proton transfer in aqueous solutions by solvation. Specific examples of similar and other synchronous reactions will be discussed below.

6. The Principal Types of Mechanisms of Acid Heterogeneous-catalytic Reactions

Since a great variety of mechanisms of acid heterogeneous-catalytic reactions follows from the foregoing, it is useful to discuss them, having combined them into individual groups, as a function of the presence or absence of solvation effects and as a function of the proton affinity of the reacting molecules. Our aim here is not to provide an exhaustive survey of the literature, because this is impossible within the framework of the present review, and we shall consider only certain most typical examples.

(a) Low-temperature Catalytic Reactions with Participation of Polar Molecules

The mechanism of low-temperature heterogeneous-catalytic reactions involving polar molecules, for example, the hydration of olefins to alcohols, the esterification of alcohols, the hydrolysis of esters, etc., is closest to the mechanism of homogeneous acid catalysis. If the reaction temperature is not too high and there is a possibility of the formation of associated species comprising several molecules, then effects analogous to the solvation effects with participation of polar molecules in solutions come into force and the protonated forms of the substrate play the role of the active intermediates in catalytic reactions. This situation resembles very strongly homogeneous catalysis in aqueous solutions, where solvation effects make a decisive contribution to the formation of protonated states and to proton transfer to the adsorbed molecules. More precisely, this is two-dimensional homogeneous catalysis in a thin liquid film condensed on the surface of the heterogeneous catalyst. In particular, the possibility of the operation of such a mechanism in the olefin hydration reaction has been demonstrated by Chirkov, Vinnik, and co-workers.[89]

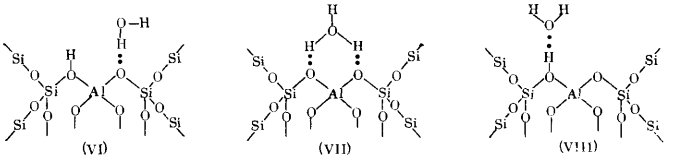
Apparently an analogous mechanism also obtains in enzyme catalysis. Here, however, the specificity of the interaction of the water or substrate molecules with the polar groups on the biopolymer surface is manifested. This leads to structure formation in the adsorbed film, which affects both the solvation energy and the proton transfer mechanism.[21–23] This factor does not, however, alter the main features—the real existence of intermediate protonated states in these systems.

(b) Heteroisotope Deuterium Exchange Reactions

Another limiting case is that of catalytic reactions involving nonpolar molecules having a minimal proton affinity. As can be seen from the Table, these include molecular hydrogen and the paraffins. Since the solvation effects are virtually absent here and the proton affinity is low, the formation of intermediate protonated states is extremely unfavourable. At the same time different versions of synchronous or joint mechanisms operate.

For a series of heteroisotope exchange reactions, their possibility has been confirmed by quantum-chemical calculations carried out using the cluster models of Brønsted acid centres examined above. In particular, synchronous heteroisotope exchange between terminal silanol groups on the silica surface and molecular deuterium can proceed via a symmetrical tetragonal transition state.[54]

The advantage of such synchronous mechanisms in the heteroisotope exchange reaction with water molecules, which have a much higher proton affinity (~7 eV), was more unexpected.[90,91] Quantum-chemical calculations have been performed for the adsorption of water and the mechanism of the heteroisotope exchange between the acid bridging hydroxy-groups in the hydrogen-forms of zeolites and water.[91] Among the three versions of the adsorption of H_2O molecules examined [structures (VI)–(VIII)], the highest heat was obtained for the interaction of water with the basic oxygen of the aluminium–oxygen tetrahedron [70 kJ mol^{-1}, structure (VI)], while the lowest heat was found for its two-point adsorption [40 kJ mol^{-1}, structure (VII)]. The heat of adsorption of water on the proton of the bridging hydroxy-group proved to have an intermediate value [46 kJ mol^{-1}, structure (VIII)].



Bearing in mind that the highest heat of adsorption corresponds to the structure (VI), one may conclude that the rate-limiting stage in the hetero-exchange is most likely to be the desorption of water from the surface. On the other hand, the reaction itself apparently proceeds via a synchronous mechanism, in the transition state (VII)

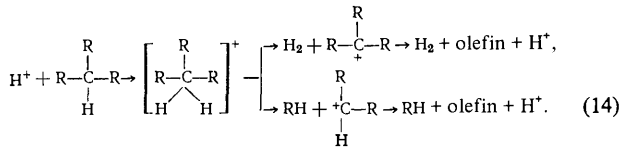
of which there is simultaneous proton transfer from the acid bridging hydroxy-group to the adsorbed water and the abstraction from it of a second proton, which is transferred to a neighbouring basic oxygen atom.

A synchronous mechanism has also been proposed for the heteroisotope exchange between surface hydroxy-groups and acetylene.[92] However, this mechanism is unlikely in the heteroisotope exchange with ethylene, whose rate is much lower.[93,94]

(c) The Cracking of Paraffins

Paraffins constitute another class of compounds in the reactions of which the formation of intermediate protonated states is unlikely because of the low proton affinity. Until recently, it was assumed that their acid-catalytic cracking proceeds via a chain mechanism and that chain transfer is achieved via the transfer of a hydride ion from the paraffin molecule to the adsorbed carbenium ions. It has been suggested that the source of the latter is olefins, which are either present in the starting material as an impurity or are formed in the dehydrogenation of the paraffins.[32]

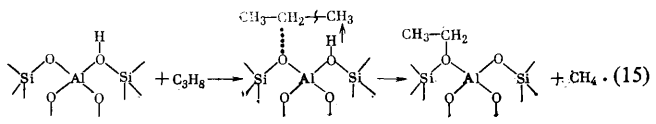
Apart from this classical cracking mechanism, which is valid at relatively low temperatures and high pressures of the hydrocarbons, there is a possibility also of protolytic cracking with participation of non-classical carbenium ions containing pentacoordinate carbon atoms:[95]



(14)

Its distinctive features are the rapid deuterium–hydrogen exchange involving the paraffins without their skeletal isomerisation and the presence of molecular hydrogen and of light C_1 and C_2 paraffins in the cracking products.

However, in conformity with what has been said above, the formation of non-classical carbonium ions as stable intermediates hardly occurs owing to the low proton affinity of the paraffins. It is sufficient to state that non-classical carbonium ions cannot be observed even in the interaction of paraffins with superacids.[70] From our point of view, an alternative synchronous cracking mechanism, involving a six-membered transition state with simultaneous proton transfer to the CH_3 group, the dissociation of a C–C bond in the paraffin molecule, and the formation of a new carbon–oxygen bond is more probable:

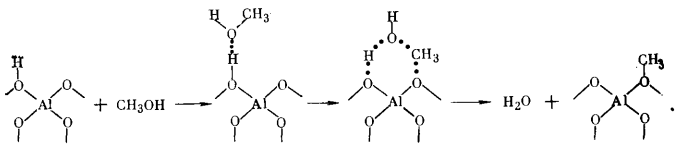


(15)

In this case the activated complex does not indeed resemble the non-classical carbenium ion but it is not a stable intermediate structure which really exists.

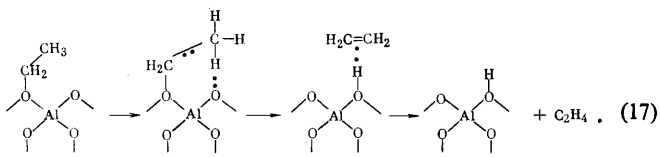
(d) High-temperature Catalytic Reactions of Alcohols

Esterification reactions, dehydration reactions with formation of olefins, alkylation of olefins and aromatic compounds by alcohols, and the synthesis of higher hydrocarbons from alcohols are characteristic high-temperature acid-catalytic reactions of alcohols. There is no doubt that, under the conditions of heteogeneous acid catalysis, the first stage in all these reactions is the formation of surface alkoxy-structures. The mechanism of this elementary stage can be treated, by analogy with heteroisotope exchange reactions between highly acid hydroxy-groups and water molecules, as a synchronous substitution reaction with participation of neighbouring basic centres and involving the inversion of the methyl group in the transition state similarly to what happens in the thoroughly investigated S_N2 nucleophilic substitution reactions



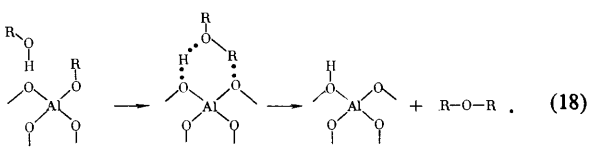
(16)

In the case of higher alcohols, the decomposition of surface alkoxy-fragments leads to the desorption of olefins from the surface:



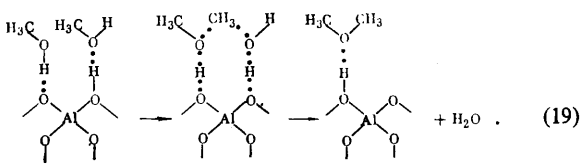
(17)

and their interaction with a second alcohol molecule results in esterification:



(18)

Another bimolecular synchronous mechanism, involving the formation of an eight-membered cyclic transition state, has also been discussed for this reaction:[90,96]



(19)

The low energy barriers in these elementary stages can be explained by the synchronous nature of the dissociation of old and the formation of new bonds in the activated complexes arising by the interaction of alcohol molecules with the surface acid–base pairs.

The establishment of the mechanism of the reactions involving the alkylation of olefins and the aromatic compounds by alcohols and also the synthesis of higher hydrocarbons from alcohols constitute a

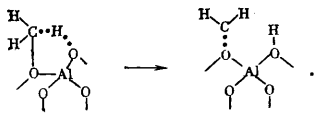
more complex problem. We shall discuss these questions below in relation to the catalytic reactions of methanol on high-silica type ZSM-5 zeolites.

Much attention has been devoted recently to the synthesis of hydrocarbons from methanol (see, for example, the relevant reviews[97,98]). The most difficult question is that of the mechanism of the formation of ethylene from methanol and of the appearance of the primary C–C bond. A wide variety of schemes involving the formation of oxonium ions, ylides, free radicals, and carbenes have been discussed in the literature,[99] the greatest preference being given to carbenes. For example, it has been suggested[32] that the methanol adsorbed on the zeolite surface loses water with formation of adsorbed carbenoid species, which then polymerise to olefins:

$$HCH_2{-}OH \rightarrow H_2O + {:}CH_2,$$
$$n{:}CH_2 \rightarrow (CH_2)_n. \qquad (20)$$

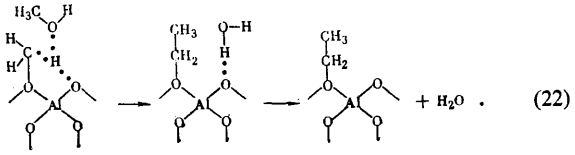
Similar mechanisms have been examined also in other investigations.[100–102]

Quantum-chemical calculations have thrown some light on this question.[69,103,104] It has been found that the properties of the surface methoxy-structures themselves are dual to some extent, combining the features of both adsorbed carbenium ions and carbenes. This is caused by the presence of a bond between one of the hydrogen atoms of the methoxy-group and the neighbouring basic oxygen atom, which undoubtedly indicates the possibility of proton transfer to the latter. This tendency increases with increase in the length of the ether bond. Although, according to calculations by the MNDO method and non-empirical calculations in terms of the STO-3G basis set there is a deficiency of approximately 1.5 eV of energy for the complete proton transfer with formation of an adsorbed carbene species and an acid hydroxy-group, i.e.



(21)

the formation of a carbene-like transition state may be significantly facilitated by the interaction with a second methanol molecule, similarly to the situation arising when the interaction with a second water or alcohol molecule favours proton transfer and the formation of ion pairs in homogeneous systems. Such transition state is then converted into a surface ethoxy-group and an adsorbed water molecule:



(22)

The ethoxy-fragment can then be alkylated by further methanol molecules via an analogous mechanism, affording the isopropoxy- or t-butoxy-structure or decomposing with desorption of ethylene.

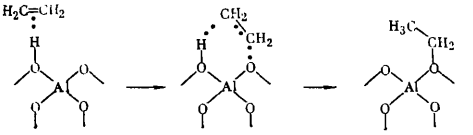
This mechanism is also synchronous, because the abstraction of a proton from the methoxy-group takes place simultaneously with formation of a new bond in the water molecule, while the dissociation of the C–O bond in the methanol molecule is compensated by the formation of a carbon–carbon bond in the alkoxy-fragment. It too has features in common with simultaneous proton transfer to two water or alcohol molecules in homogeneous systems with the sole difference that the additional energy source is in this instance not the heat of solvation of the intermediate protonated state but the energy evolved as a result of the chemical alkylation reaction.

The carbene-like properties of methoxy-groups on the surfaces of high-silica zeolites has been confirmed experimentally.[105] It was found that the interaction of the surfaces of previously methoxylated ZSM-5 zeolites with benzene, ethane, and propane, entails the incorporation of methylcarbene fragments into these molecules, which leads to the formation of toluene, propane, and butane.

(e) Catalytic Reactions of Olefins

Double bond migration, skeletal isomerisation, polymerisation, and cracking reactions are characteristic catalytic reactions of olefins in the presence of heterogeneous catalysts of the acid type. Adsorbed carbenium ions are traditionally considered as the active intermediate structures in all these reactions. In conformity with the foregoing, it is more correct, however, to speak of the formation of surface alkoxy-fragments or esters, whose carbenium ion properties are manifested only in transition states with extended or vibrationally excited C–O bonds.

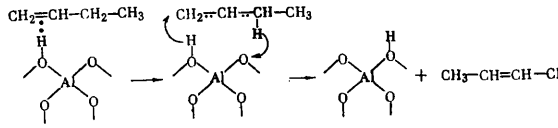
In the interaction of olefins with acid hydroxy-groups, hydrogen-bonded complexes are formed initially. This is followed by the two-point adsorption of the olefin, which, to coin a phrase, "creeps off" to a neighbouring basic centre, being converted into a surface alkoxy-group:



(23)

The reverse process leads to the desorption of olefins. The migration of the double bond in olefins and deuterium exchange involving them can also be explained by the reversibility of reaction (23).

Such multistage (but concerted as regards the elementary proton transfer step) mechanism does not, however, rule out the possibility of the migration of the double bond also via a synchronous mechanism without the formation of stable intermediate protonated states:[62]



(24)

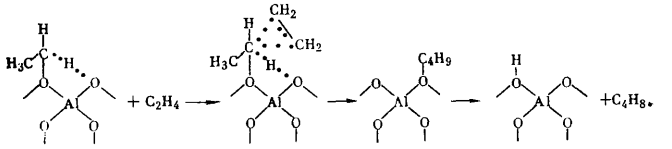
A concerted mechanism of the isomerisation of olefins is more probable for reactions involving moderately acid hydroxy-groups, while the multistage mechanism is preferable in the case of highly acid Brønsted centres.

We shall now discuss the mechanism of the oligomerisation of olefins. It is generally accepted that this reaction proceeds with the participation of adsorbed carbenium ions, which are readily formed from branched olefins but not from ethylene.[34] From our point of

view, this claim must be understood in the sense that the ease of formation of carbenium ion transition states from covalent alkoxy-structures increases with increase in the degree of their branching.

This tendency has been traced[106] with the aid of quantum-chemical calculations for methyl, ethyl, and isopropyl fragments adsorbed on the surfaces of high-silica zeolites. It was found that, although their positive charges are virtually identical, the tendency towards heterolytic dissociation diminishes on passing from the isopropyl to the ethyl substituent. The carbenium ion mechanism, which is characteristic of the oligomerisation of higher olefins, is ineffective in the case of ethylene.

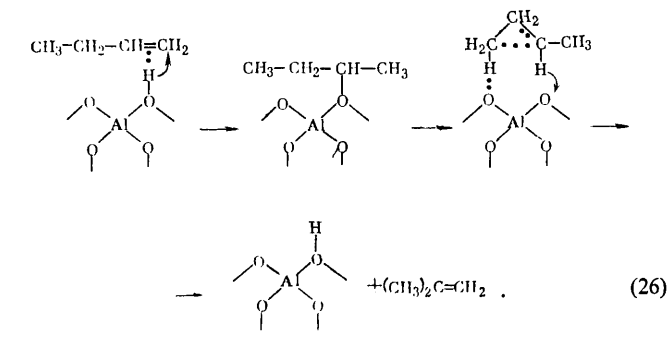
If, on the other hand, account is taken, by analogy with the previously discussed Scheme (21), of the fact that the abstraction of α-protons from the ethyl fragments imparts properties of adsorbed ethylcarbenes to the latter, presumably the oligomerisation of ethylene can also proceed via the "carbene" mechanism in certain cases:[107,108]



(25)

The transition state resembles in this instance cyclopropane or its derivatives. On the other hand, the source of the additional energy compensating for the difficulty forming the carbene-like activated complex is, as in the reactions of methanol discussed above, a chemical reaction, and in this case it is the oligomerisation reaction and not the alkylation reaction. The reverse reaction leads to the cracking of olefins.

It may be that the skeletal isomerisation of olefins proceeds also via an analogous "cyclopropane" transition state formed when γ-protons are split off from the surface alkoxy-groups:



(26)

Thus the generally accepted mechanism of the carbenium ion reactions of olefins under the conditions of heterogeneous acid catalysis can be usefully supplemented by two new elementary reactions which take into account the dual carbenium ion and ylide nature of the transition states formed from covalent alkoxy-structures:

(1) The elimination of a proton from the α-carbon atom, which leads to the possibility of alkylation and oligomerisation reactions via the ylide mechanism, which is an alternative to the carbenium ion mechanism.

(2) The elimination of a proton from the γ-carbon atom, which leads to the skeletal isomerisation and cracking of olefins.

Since the cracking and skeletal isomerisation proceed via the same cyclic cyclopropane transition state, these reactions should take place under similar conditions and on the same active centres.

The conclusions concerning the composition of the products of the corresponding catalytic reactions, made on the basis of the ideas developed above, hardly differ from those which follow from the chemistry of carbenium ions. At the same time, the schemes which we have proposed are much more realistic than those discussed in the literature, because they take into account the interaction of the active intermediate species with the surface. Furthermore, they make it possible to understand what are the driving forces and causes of the selectivity or relative ease of particular elementary stages of heterogeneous acid-catalytic reactions.

IV. CONCLUSION

The results described show that, apart from the analogies between homogeneous and heterogeneous acid catalysis frequently discussed in the literature, there are also significant differences between these types of catalytic action. The main one is the absence of solvation effects in high-temperature catalytic reactions of hydrocarbons. For this reason, many heterogeneous acid-catalytic reactions do not proceed via ionic intermediate compounds, which are energetically unfavourable under these conditions, but via a synchronous mechanism which makes it possible to avoid their formation. Thus the main disadvantage of the modern ideas about the mechanisms of heterogeneous-catalytic reactions is the formal description of these mechanisms within the framework of a single multistage ionic scheme. In fact, depending on the proton affinity of the reacting molecules and also on the presence or absence of solvation effects, a broad range of different mechanisms operate. Their range extends from homogeneous catalysis in thin liquid films condensed on the surfaces of heterogeneous catalysts to a synchronous reaction with the participation of acid-base pairs, where stable intermediate protonated states are not produced.

Another disadvantage of modern theoretical ideas in the field of heterogeneous acid catalysis is the failure to take into account the interaction of protonated intermediate structures with the catalyst surface. The contribution of this factor to the energetics of proton transfer is in fact very significant and in many cases decisive. The interaction of weakly basic organic molecules with Brønsted acid centres therefore leads to the formation in most instances of covalent surface intermediate compounds and not of quasi-free carbenium ions. On the other hand, the properties of carbenium ions are manifested in transition states where the carbon–basic oxygen bond on the catalyst surface is partly dissociated (extended or vibrationally excited).

Finally yet another feature of heterogeneous acid catalysis is the bifunctional nature of its active centres, the acid part of which is a proton donor while the basic part either stabilises the intermediate protonated compounds or promotes the elimination of a proton from the transition states in the synchronous reaction mechanisms. Deprotonation can impart also the features of adsorbed carbenes or ylides to the activated complexes. Allowance for this factor permits a more natural explanation of the mechanisms of the reactions involving the alkylation, cracking, and skeletal isomerisation of olefins. Incidentally, all that has been said applies equally and in general to electrophilic reactions in organic chemistry, while allowance for the interaction of intermediate protonated structures with

counterions is also an essential condition for the correct interpretation of the reaction mechanisms. However, the discussion of these questions is outside the framework of the present review.

The ideas developed above should not be regarded as a criticism of the concept of carbenium and carbonium ions in heterogeneous acid catalysis. The aim is rather to deepen and update this concept. Naturally, many of the mechanisms discussed are so far debatable and their confirmation requires further quantum-chemical calculations for detailed kinetic and spectroscopic studies.

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The Phase Boundary Potentials at the Interface between Two Immiscible Electrolyte Solutions

V.S.Markin and A.G.Volkov

The theoretical aspects of the calculation and measurement of the interphase [phase boundary] potential difference at the interface between two immiscible liquids are examined and the non-thermodynamic tetraphenylborate hypothesis, which makes it possible to determine the standard ion distribution potentials, is discussed. The electrochemical properties of charged interfaces are analysed and equations are presented for the interphase potential jumps in the presence of Donnan equilibrium, incomplete dissociation of the salt, two electrolytes with a common ion, complex formation in one of the phases, and an oxidation-reduction equilibrium. The experimental methods for the measurement of the interphase potential difference and for testing the thermodynamic theory of distribution potentials at reversible interfaces are examined
The bibliography includes 93 references.

CONTENTS

I. Introduction 1124
II. Interfaces 1124
III. Interphase potentials 1127
IV. Measurement of interphase potential jumps 1133
V. Test of the thermodynamic theory of interphase potentials 1139

I. INTRODUCTION

One of the fundamental problems in modern chemistry involves the elucidation of the mechanism of the distribution of charges at the interface between two immiscible liquids. The solution of this problem is essential for the development of phase-transfer and surface catalysis, electrochemistry and colloid chemistry, artificial photosynthesis and biochemistry, improvement of extraction processes, and the creation of ion-selective electrodes.

The electrochemistry of the interface between two immiscible electrolyte solutions developed significantly only in the last century. However, despite major advances, there are many obscure aspects and unsolved problems in this branch of physical chemistry. In the present review, an attempt is made to describe the main properties of charged interfaces between two immiscible electrolyte solutions.

As at any interface, a difference between electrical potentials arises at the interface between two immiscible liquids which in the case of equilibrium systems is called the boundary potential difference or briefly the boundary potential.[1]

The controversy concerning the nature of the potential jumps at the interface between two immiscible electrolyte solutions dates back to the beginning of the century.[2] Despite its apparent simplicity, this problem remains of current interest.[3-6] Some workers[7,8] have transferred, without adequate justification, the Donnan theory,[9] developed for the calculation of the potential differences between electrolyte solutions in two identical solvents α and α', differing only in the ionic composition, to the system of two arbitrary immiscible liquids α and β. The potential difference $\Delta_{\alpha}^{\alpha}\cdot\varphi$ between two identical phases α and α' is a thermodynamically measurable quantity. On the other hand, $\Delta_{\beta}^{\alpha}\varphi$ at an oil-water interface cannot be measured from the standpoint of thermodynamics but it can be estimated on the basis of model considerations.[3,4,10-14] The error associated with it, which was introduced in the above study,[7] led to the derivation of an incomplete formula for the Donnan potential, which is valid only in certain special cases for phases of identical nature. Unfortunately, this inaccuracy spread from the above study[7] to certain reviews[8] and has created the illusion that a purely thermodynamic determination of the Galvani potential difference is possible.

Finally, interphase oxidation-reduction potentials have been examined in the literature solely for certain special systems,[10,12,15] although it is undoubtedly important to give a general definition of this concept.

In the present reivew, an attempt is made to fill these gaps and to arrange systematically the definitions and formulae used to estimate interphase potentials.

II. INTERFACES

1. The Structure of Interfaces

If two pure liquids are placed in a vessel, then, depending on their physicochemical properties, there is a possibility of the formation of several types of structures. If the molecules of each liquid can interpenetrate one another, mixing in any proportions, such liquids can be called ideally miscible. Naturally, it is then impossible to obtain a potential difference between the two phases. An example of such a system is the well known water-ethanol pair. If the molecules of neither liquid can penetrate into the other, then such liquids can be referred to as ideally immiscible. Either a sharp boundary or a transitional layer, in which components from both phases are present, is established between them. An example of two ideally immiscible liquids is the mercury-water system. Sometimes the interface between two liquids is represented arbitrarily by a mathematical surface without thickness. This is an ideal boundary for which the term "interface" is used in the English language literature. However, in reality at the molecular level it is impossible to draw a sharp boundary between two phases. A transitional layer (interphase), whose properties differ from those of the phases in contact, is formed in this region. The thickness of the transitional

layer is $\sim 0.1-10$ nm. In this connection, it must be emphasised that the extremely convenient concept of the ideal boundary is a model one and is therefore outside the framework of thermodynamics.

This review is devoted to the electrochemistry of the interface between two immiscible liquids or more precisely two liquids with limited miscibility, an example of which may be an oil–water system: both phases are sparingly soluble in one another and there is an interface between them, constituting a transitional layer in which the properties of the medium vary from those of one phase to those of the other. The miscibility of the liquids in the most thoroughly investigated oil–water systems is low, being of the order of hundredths per cent (if nitrobenzene, dichloroethane, octane, or decane is used as the organic phase).

2. Polarisable and Non-polarisable Interfaces

The interfaces between two immiscible electrolyte solutions are characterised by polarisabilities of different types depending on the extent to which they are permeable to the charged species present in the system.[16–20] Since formulations which are not completely accurate are frequently encountered in the literature, we shall consider briefly this question.

If the charged species cannot pass through the interface, the latter is referred to as polarisable; otherwise the boundary is called non-polarisable or reversible. We shall begin the discussion with polarisable boundaries. Since any boundary is to some extent permeable to ions, in practice one has to speak only of a particular degree of approximation to the limiting version of polarisable boundaries. This limiting version is frequently referred to in modern literature as an ideally polarisable boundary. In the IUPAC recommendations,[16] a boundary between two phases is called polarisable if the phases contain no components in common or if the exchange of the components is difficult. As will be shown below, this definition is unsatisfactory, because, when the conditions indicated are fulfilled, there is a possibility of situations in which a direct current flows across the interface.

Next it is stated in the above recommendations that the interface can be divided into two components containing respectively charged species from the phases α and β only. This model idea, which constitutes a drastic simplification of the real situation, actually restricts the scope of the investigation of polarisable boundaries, reducing them to a single special case. Other versions, which can be realised in specific systems, escape the investigator's attention. Incidentally, the authors of the recommendations[16] agree that many of their definitions are based on specific models, stipulating this already in the first page of their report.

The use of specific models is not open to objection when this is necessary, but we believe that attempts to define a general thermodynamic property in terms of specific models is illegitimate because this deprives the property described of the necessary generality. However, as pointed out by Frumkin,[21,22] such simplification of the problem is not, in principle, necessary, because in this field a system of definitions not employing specific model concepts has existed for a long time. As early as 1891, Planck[17] introduced the rigorous thermodynamic concept of a completely polarisable boundary. He defined it as the "boundary whose state is fully defined by the charge passed through it starting from a certain instant".

In the first place, it follows from this formulation that the Planck definition fully excludes the possibility of the passage of a direct current through the boundary since otherwise the state of the boundary would no longer depend on the charge passed through it. The current may flow between the phases only in a transient regime. In this definition, nothing is said about the way in which the charged species which have arrived from different phases are distributed in the transitional layer. Their distribution may be of any kind and, in particular, they can overlap (Fig.1). Such a situation can arise on metallic electrodes when there is partial or complete electron transfer to adsorbed ions or from these ions to the metal. However, charge transfer between the bulk phases is impossible in the presence of a completely polarisable boundary.

A special case of a completely polarisable boundary is the ideally polarisable boundary whose underlying concepts have been formulated by Koenig.[18] Fig.1*b* illustrates the structure of Koenig's ideally polarisable boundary. There is a transitional layer between homogeneous phases α and β whose properties vary from those of the phase α to those of the phase β. In the transitional layer, the phases are arbitrarily divided by Koenig's surface which is impermeable to all charged species (both ions and electrons). This surface constitutes an infinitesimally narrow and infinitely high energy barrier for all charged species, which in fact constitutes the difference between ideally polarisable and completely polarisable boundaries. It is in principle unimportant in this case which charged species enter into the composition of each phase. Koenig's definition is outside the framework of thermodynamics, since a definite structure of the interfacial region is postulated in it and non-thermodynamic assumptions concerning the existence of an infinitely high energy barrier for all the charged species are used.

Although the concept of the ideally polarisable electrode was developed by Koenig in 1934, the term ideally polarisable boundary (or electrode) as such was introduced later[19] and Koenig himself[18] used Planck's term. The term "ideally polarisable boundary" has been used in modern literature in a somewhat loose sense starting from Grahame's review.[20] It frequently includes the concepts of both an ideally polarisable boundary and of a completely polarisable boundary. It is sufficient to say that such confusion occurs even in the "electrochemical nomenclature" recommended by IUPAC.[16] Since Grahame[20] did not differentiate the concepts of free and thermodynamic surface charges and did not consider the adsorption or local charge transfer at the interface, he assumed that there is no need to use Koenig's surface in order to introduce the concept of the ideally polarisable electrode. Many investigators repeat this error to the present day, although as early as two decades ago Frumkin and co-workers[21,22] analysed in detail the difference between ideally and completely polarisable electrodes. It was shown that a completely polarisable electrode can include, in contrast to an ideally polarisable electrode, systems with local or adsorption charge transfer. For example, at a platinum electrode, whose potential is more positive than the equilibrium hydrogen potential by up to 300 mV, hydrogen ions are adsorbed from solution, react with the electrons from the metal, and form adsorbed hydrogen atoms:

$$H_{ads} \rightleftarrows H^+ + e^-.$$

This reaction is rapid on platinum and, starting from a certain instant, can be regarded as reversible. Although local charge transfer occurs here and Koenig's surface cannot be introduced,

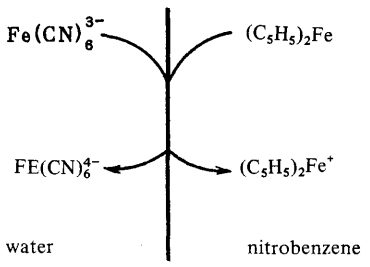
there is no charge transfer between the phases and the electrode is completely polarisable as defined by Planck but not ideally polarisable as defined by Koenig.

If the phases α and β contain even one common ion, which moves freely across the interface, then such an interface can be referred to as reversible or non-polarisable. Despite the fact that the latter term is generally accepted, it does not reflect quite accurately the state of the system. A reversible (non-polarisable) interface can be partly polarisable or completely non-polarisable. Large currents can flow in either direction across a completely non-polarisable interface between two phases containing at least one common ion without causing a deviation of the interphase potential difference from the equilibrium value. Ideally polarisable and completely non-polarisable interfaces do not exist in nature, although certain electrodes can have properties close to ideality under certain conditions.

A partially polarisable interface corresponds to the intermediate state between ideally (completely) polarisable and non-polarisable interfaces. This difference actually exists and is usually investigated in electrochemistry.

In conclusion, we shall show that the definition proposed by IUPAC,[16] namely that the boundary between phases should be regarded as ideally polarisable when the phases contain no common components or the exchange of the components is difficult and cannot be regarded as satisfactory.

Suppose that a lipophilic reductant and a hydrophilic oxidant have been added to a water–oil system where each phase contains electrolytes (but there are no common ions in the two phases), so that an electron exchange reaction takes place at the interface:



In this case the interface ceases to be ideally polarisable and becomes partly polarisable or non-polarisable depending on the reaction conditions, although the oil and water contain no common ions. One can foresee the objection that electrons can be regarded as a common component in the two phases although they are not present in them in a free form. However, this does not save the IUPAC definition[16] because it vitiates the significance of its first part: "...when the phases contain no common components".

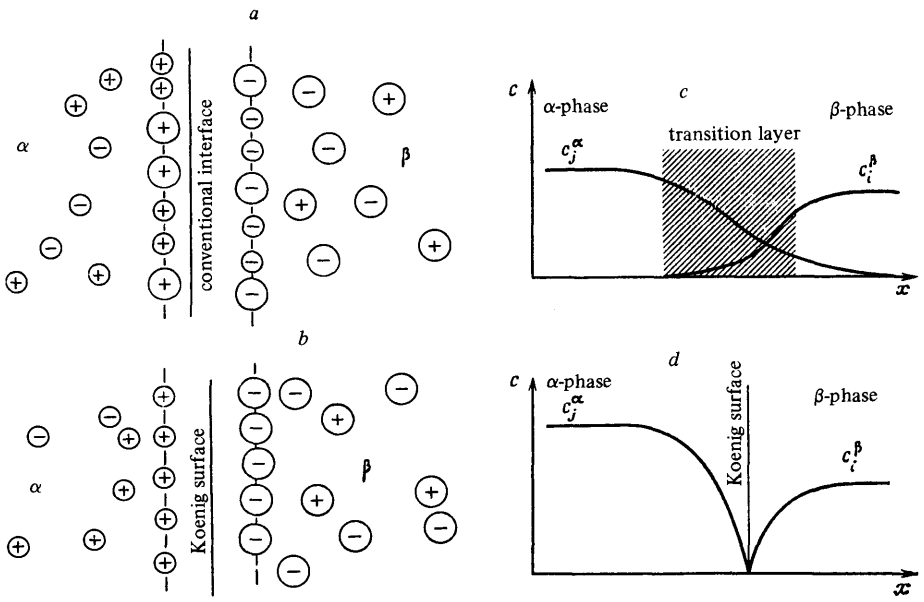


Figure 1. Schematic illustration of the distribution of ions and of the structure of the completely (*a*, *b*, *c*, and *d*) and ideally (*b* and *d*) polarisable interfaces.

III. INTERPHASE POTENTIALS

1. Boundary Potentials

As at any interface, an electrical potential difference is established at equilibrium at the interface between two immiscible liquids, which is referred to as the boundary potential difference or, briefly, the boundary potential. A classification of interphase potential jumps was introduced in 1930.[23] Fig.2 illustrates schematically the interphase potential jumps at the boundary between two immiscible phases, α and β, and also between these phases and the vacuum. The potential Ψ^{α}, measured *in vacuo* in the immediate vicinity of the above surface, is referred to as the Volta potential or the external potential. The potential φ^{α}, in the bulk of the phase, reckoned relative to a point in a vacuum at an infinite distance, is referred to as the Galvani potential or the internal potential. These two potentials differ by the surface potential jump χ^{α}.

In a study of the contact between the phases α and β, the Galvani potential difference

$$\Delta_{\beta}^{\alpha}\varphi=\varphi^{\alpha}-\varphi^{\beta},$$

which is determined by the specific distribution of the charged and polarised dipolar species in the vicinity of the interface, is of principal interest. The dipolar component of the interfacial potential difference $\Delta_{\beta}^{\alpha}\varphi_h$ is sometimes separated from the overall difference between the Galvani potentials; one can then obtain the quantity

$$\Delta_{\beta}^{\alpha}\varphi-\Delta_{\beta}^{\alpha}\varphi_h,$$

which is determined by the distribution of ions. Such separation is of practical value in those cases where the dipolar contribution to the potential jump is independent of the overall interphase potential difference (or depends only slightly on the latter), i.e. is ultimately independent of the ionic potentials and one can assume that all the changes in the interphase potential difference are described solely by the ionic contribution (the measurement and calculation of this contribution constitutes to a large extent the subject of the modern science of the interface between liquid electrolyte solutions). However, there is usually no certainty that the separation of the interphase potential difference into two independent components, due to the ionic and dipolar contributions, is valid and treatment of the results in such terms involves a certain degree of approximation.

One should also bear in mind that, contrary to the claim frequently encountered in the literature,[24] the dipolar potential jump $\Delta_{\beta}^{\alpha}\varphi_h$ at the interface between two immiscible electrolyte solutions is generally speaking not equal to the potential difference at the boundaries of these phases with a vacuum even in the case of specific adsorption:

$$\Delta_{\beta}^{\alpha}\varphi_h\neq\Delta_{\beta}^{\alpha}\chi=\chi^{\alpha}-\chi^{\beta}.$$

The reason is the mutual influence of the phases on the orientation of the dipolar molecules in the boundary layers of the liquid. Table 1 illustrates the thermodynamic feasibility of the experimental measurement of boundary potentials.

The equilibrium potentials at a reversible or non-polarisable interface are divided into three types depending on which species pass from phase to phase:

1. Potentials which arise in an equilibrium system where all the ions are capable of passing from one phase to the other are referred to as *distribution potentials.*

2. If the phases in contact contain ions some of which are capable of crossing the boundary while others are not, *Donnan potentials* or membrane potentials are generated. The transfer of ions may be prevented by either mechanical (as in semipermeable membranes) or chemical (as in ion exchangers) causes. If ions of only one kind can cross the interface, then the membrane potential difference is called the *Nernst potential.*

3. If two immiscible electrolyte solutions exchange electrons and are in equilibrium with respect to electrons, then an *oxidation-reduction potential* is established at the interface.

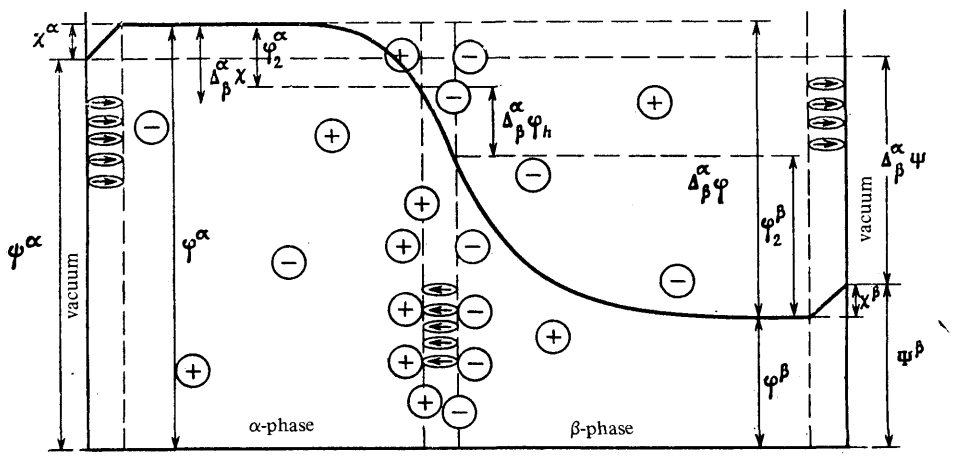


Figure 2. Boundary potentials in an oil–water system: $\psi^{\alpha}(\psi^{\beta})$—external potential or Volta potential; $\varphi^{\alpha}(\varphi^{\beta})$—internal potential of the phase α(β); $\chi^{\alpha}(\chi^{\beta})$—surface potential jump equal to the difference between φ^{α} and ψ^{α} (φ^{β} and ψ^{β}); $\Delta_{\beta}^{\alpha}\varphi$—Galvani potential difference; $\Delta_{\beta}^{\alpha}\psi$—Volta potential difference; $\Delta_{\beta}^{\alpha}\varphi_h$—the dipolar component of the interphase Galvani potential difference; φ_2^{α} and φ_2^{β}—potential jumps in diffuse layers.

Interphase potentials on completely (and ideally) polarisable boundaries can be due to the adsorption of charged or dipolar species at the interface or by the charging of the latter from an external source.

Table 1. Thermodynamic feasibility of the experimental measurement of the boundary potentials in immiscible liquid phases α and β.

Boundary potentials	Feasibility of measurement
External potential of one phase Ψ	Measured
Volta potential $\Delta_\beta^\alpha\Psi$	Measured
Surface potential χ	Not measured
Difference between surface potentials $\Delta_\beta^\alpha\chi$	Not measured, but can be determined when an additional non-thermodynamic hypothesis is used
Internal potential φ	Not measured
Difference between Galvani potentials $\Delta_\beta^\alpha\varphi$	Not measured, but if both phases have the same composition, measurement is possible
Change in $\Delta_\beta^\alpha\varphi$ during any process (adsorption, change in temperature, concentration, etc.)	Measured
Potential difference in the cell between phases of the same composition $E = \Sigma\Delta_\beta^\alpha\varphi$	Measured
Distribution potential of the salt or individual ion—$\Delta_\beta^\alpha\varphi$ or $\Delta_\beta^\alpha\varphi_i^0$	Not measured, but can be determined when an additional non-thermodynamic hypothesis is used
Change in $\Delta_\beta^\alpha\chi$ during any process (adsorption of dipoles, change in temperature, etc.)	Measured

Thermodynamics makes it possible to determine the interfacial potential only at a reversible interface. In the case of an ideally polarisable boundary, the potential is an additional independent variable characterising the state of the boundary and is specified by an external potential source. An electrostatic rather than an electrochemical equilibrium is maintained on an ideally polarisable boundary. It is analogous to the state of a charged condenser.

2. Standard Potentials and Standard Free Energies

Suppose that the phases α and β in contact contain ions I_i with a charge number z_i and an activity a_i. It follows from the condition for electrochemical equilibrium that

$$\Delta_\beta^\alpha\varphi = -\frac{\mu_i^{0,\alpha} - \mu_i^{0,\beta}}{z_iF} + \frac{RT}{z_iF}\ln\frac{a_i^\beta}{a_i^\alpha}, \quad (1)$$

where μ is the chemical potential and F the Faraday. The difference between the standard chemical potentials of the ion i in the two phases

$$\mu_i^{0,\alpha} - \mu_i^{0,\beta} \equiv \Delta_\beta^\alpha G_i^0(i) \quad (2)$$

represents the energy of transolvation or the standard Gibbs free energy $\Delta_\alpha^\beta G_i^0(i)$ of the transfer of the ion i from the phase α to the phase β. We introduce two further definitions: the distribution coefficient of the ions:

$$P_i^{\alpha/\beta} = \exp(-\Delta_\beta^\alpha G_i^0(i)/RT) \quad (3)$$

and the standard potential of the distribution of ions of the given kind:

$$\Delta_\beta^\alpha\varphi_i^0 = -\frac{\Delta_\beta^\alpha G_i^0(i)}{z_iF} \equiv \frac{RT}{z_iF}\ln P_i^{\alpha/\beta}. \quad (4)$$

According to Eqn.(3), it is evident that $P_i^{\alpha/\beta} = 1/P_i^{\beta/\alpha}$.

The interphase potential difference can be represented in the form

$$\Delta_\beta^\alpha\varphi = \Delta_\beta^\alpha\varphi_i^0 + \frac{RT}{z_iF}\ln\frac{a_i^\beta}{a_i^\alpha} \equiv \frac{RT}{z_iF}\ln\left(P_i^{\alpha/\beta}\frac{a_i^\beta}{a_i^\alpha}\right). \quad (5)$$

The equilibrium ratios of the activities of the ions i in two phases is described by the expression

$$\frac{a_i^\alpha}{a_i^\beta} = \frac{\gamma_i^\alpha c_i^\alpha}{\gamma_i^\beta c_i^\beta} = \exp\left[-\frac{z_iF}{RT}(\Delta_\beta^\alpha\varphi - \Delta_\beta^\alpha\varphi_i^0)\right] = P_i^{\alpha/\beta}\exp\left(-\frac{z_iF}{RT}\Delta_\gamma^\alpha\varphi\right), \quad (6)$$

where γ is the activity coefficient and c the concentration.

Hence the physical significance of the concepts introduced becomes clear. The standard distribution potential of the given ion represents the interfacial potential difference which would be established at the interface if the equilibrium activities of this ion in the two phases were identical. The partition coefficient of the ions $P_i^{\alpha/\beta}$ corresponds to the equilibrium ratio of the activities of the ions i in the two phases in the absence of an interphase potential difference.

It follows from the electroneutrality condition for the phases that

$$\sum_i z_ic_i^\alpha = 0; \quad \sum_i z_ic_i^\beta = 0. \quad (7)$$

The relation between the interphase potential $\Delta_\beta^\alpha\varphi$ and the concentration of ions in solutions is described by Eqns.(6) and (7). If there are n types of ions in the system, then the number of equations is $n + 2$ and the number of variables is $2n + 1$, i.e. the number of independent variables in the system is $n - 1$. In other words, it is possible to specify the concentrations of ions of all kinds in a single phase except one. The concentration of the ions of the remaining kind in this phase, the concentrations of all the ions in the other phase, and the interphase potential are then determined by solving a system of equations.

Apart from the activities of individual ions, it is convenient to use the concept of the mean activity of a 1:1 electrolyte BA:

$$a_{BA}^{\pm} = (a_Ba_A)^{1/2}. \quad (8)$$

The mean activity coefficient of the electrolyte is then given by

$$\gamma_{BA} = (\gamma_B\gamma_A)^{1/2}. \quad (9)$$

The partition coefficient of a 1:1 electrolyte can be introduced analogously:

$$P_{BA}^{\alpha/\beta} = (P_B^{\alpha/\beta}P_A^{\alpha/\beta})^{1/2}. \quad (10)$$

It is readily seen that $P_{BA}^{\alpha/\beta}$ is simply equal to the ratio of the mean activities of this electrolyte within the bulk of the phases α and β:

$$P_{BA}^{\alpha/\beta} = a_{BA}^{\pm\alpha}/a_{BA}^{\pm\beta}. \quad (11)$$

It is of interest that this ratio, in contrast ot the analogous ratio for

the individual ions [Eqn.6)], is independent of the interfacial potential. It is also independent of the presence of other ions in the solutions.

3. Distribution Potentials

(a) Fully Dissociated Electrolyte

We shall consider the simplest case where the boundary is non-polarisable and the phases α and β contain a binary 1:1 electrolyte B^+A^-:

$$\alpha,\ B^+A^-|B^+A^-,\ \beta. \tag{12}$$

The interfacial potential can be readily found from Eqn.(5) and the electroneutrality condition:

$$\Delta_\beta^\alpha\varphi = \frac{\Delta_\beta^\alpha\varphi_B^0 + \Delta_\beta^\alpha\varphi_A^0}{2} + \frac{RT}{2F}\ln\frac{\gamma_B^\beta\gamma_A^\alpha}{\gamma_A^\beta\gamma_B^\alpha}. \tag{13}$$

The first term reflects the individual characteristics of the ions in two media in the standard state, while the second depends on the activity coefficients, i.e. reflects the concentration effects. However, in practice the activity coefficients of the cation and anion can be regarded as approximately identical: $\gamma_A^\alpha \simeq \gamma_B^\alpha$ and $\gamma_A^\beta \simeq \gamma_B^\beta$. The expression for the interphase potential difference then assumes the simple form

$$\Delta_\beta^\alpha\varphi = \frac{\Delta_\beta^\alpha\varphi_B^0 + \Delta_\beta^\alpha\varphi_A^0}{2} \equiv \frac{RT}{2F}\ln\frac{P_B^{\alpha/\beta}}{P_A^{\alpha/\beta}}. \tag{14}$$

Thus the interphase potential difference is equal to the arithmetical mean of the standard distribution potentials of the individual ions. This potential difference between the two phases in the presence of a binary electrolyte has been called the distribution potential.[2,25] In this approximation, the distribution potential is independent of the concentration of the electrolyte BA. It is also independent of the structure of the interface, because it is determined solely by the thermodynamic properties of the bulk phases. This rule has been confirmed by experimental studies (see Section 5), although under certain conditions deviations from it occur. At low concentrations of the salt BA, the interphase potential difference depends also on the presence of other ions into which the solvent molecules dissociate and also of HCO_3^- ions if the measurements are performed in air and not in an inert gas.

When the number of ions in the system is greater than two, the distribution potential is known to depend on the concentrations of the ionic component of the system. The structure of the interface between two immiscible electrolyte solutions is also determined by the volume properties of the phases in contact. If a monolayer of a surfactant almost insoluble in both phases is adsorbed at the interface, then formally this should not alter the value of $\Delta_\beta^\alpha\varphi$ determined from Eqn.(13). However, the blocking of the surface by the surfactant molecules may disturb the thermodynamic equilibrium, as a result of which the measured potential difference ceases to correspond to the equilibrium value and differs from the distribution potential. The interphase potentials at an interface between two immiscible electrolyte soslutons have been calculated in different specific situations.[11,22,26]

One may consider the general case of an asymmetric electrolyte:

$$\alpha,\ B_p^{k+}A_t^{l-}|B_p^{k+}A_t^{l-},\ \beta. \tag{15}$$

In this case, the interphase potential, determined by the distribution of electrolytes between two phases, is described by the expression

$$\Delta_\beta^\alpha\varphi = \frac{z_B\Delta_\beta^\alpha\varphi_B^0 - z_A\Delta_\beta^\alpha\varphi_A^0}{z_B - z_A} + \frac{RT}{(z_B - z_A)F}\ln\frac{\gamma_B^\beta\gamma_A^\alpha}{\gamma_B^\alpha\gamma_A^\beta}. \tag{16}$$

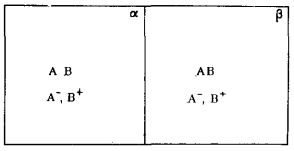
For an asymmetric electrolyte, the partition potential depends on the salt concentration. The second term on the right-hand side of Eqn.(16) is given by the following expression according to the Debye–Hückel theory:

$$\frac{RT}{(z_B - z_A)F}\ln\frac{\gamma_B^\beta\gamma_A^\alpha}{\gamma_B^\alpha\gamma_A^\beta} \simeq (z_B + z_A)\frac{e_0^3\sqrt{125\,N_A^3}}{2\pi F\varepsilon_0^{3/2}\sqrt{RT}}\left(I_\alpha^{1/2}\varepsilon_\alpha^{-3/2} - I_\beta^{1/2}\varepsilon_\beta^{-3/2}\right),$$

where I_α is the ionic strength of the solution in the phase α, N_α the Avogadro number, ε_0 the electrical constant, and ε_α the dielectric constant of the phase α. In terms of the Debye approximation, the distribution potential is independent of concentration only for a symmetrical electrolyte, where $z_A = -z_B$.

4. Incomplete Dissociation of the Salt

With the aid of the scheme



we shall consider the question of how the incomplete dissociation of the electrolyte can be reflected in the interphase distributions.

Suppose that the reaction

$$B^+ + A^- \overset{K_{BA}^\alpha}{\rightleftarrows} BA, \tag{17}$$

where K_{BA}^α is the dissociation constant of the BA molecule, takes place in the phase α. This means that the equality

$$a_B^\alpha a_A^\alpha = K_{BA}^\alpha a_{BA}^\alpha. \tag{18}$$

holds at equilibrium. The dissociation constant K_{BA}^α is related to the chemical potentials μ of the corresponding species by the equation

$$RT\ln K_{BA}^\alpha = \mu_{BA}^{0,\alpha} - \mu_{B^+}^{0,\alpha} - \mu_{A^-}^{0,\alpha}, \tag{19}$$

where μ^0 is the standard chemical potential. The same equations can be written for the dissociation in the β-phase.

The undissociated BA molecules can be distributed between the phases and the partition coefficient $P_{BA}^{\alpha/\beta}$ is defined by the equation

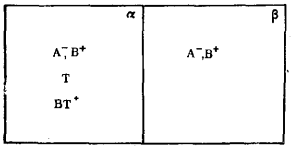
$$RT\ln P_{BA}^{\alpha/\beta} = \mu_{BA}^{0,\beta} - \mu_{BA}^{0,\alpha}. \tag{20}$$

The incomplete dissociation of the molecules does not affect the interphase potential. A distribution potential, defined by Eqn.(5), is established at the boundary. The standard distribution potentials of individual ions [Eqn.(4)] also do not change. However, owing to the presence of the dissociation equilibrium and the distribution of the undissociated molecules between the phases, a relation arises between the constants of these processes and the difference between the standard Gibbs free energies of the ions (and hence also the standard potentials):[26]

$$RT \ln \frac{K_{BA}^{\beta}}{K_{BA}^{\alpha} P_{BA}^{\alpha/\beta}} = \Delta_{\beta}^{\alpha} G_{B+}^{0} + \Delta_{\beta}^{\alpha} G_{A-}^{0} = F\Delta_{\beta}^{\alpha}\varphi_{A-}^{0} - F\Delta_{\beta}^{\alpha}\varphi_{B+}^{0}. \quad (21)$$

5. Complex Formation in One of the Phases

Suppose that the binary electrolyte BA is distributed between the phases α and β and that the phase α contains in addition a neutral complexone T which can combine with the cation B^+ to form the charged complex BT^+:



The reaction

$$B^+(\alpha) + T(\alpha) \overset{K_{BT}^{\alpha}}{\rightleftarrows} BT^+(\alpha). \quad (22)$$

takes place in the phase α and the dissociation constant K_{BT}^{α} is defined by the equation

$$RT \ln K_{BT}^{\alpha} = \mu_{BT+}^{0,\alpha} - \mu_{B+}^{0,\alpha} - \mu_{T}^{0,\alpha}. \quad (23)$$

Apart from the homogeneous dissociation constant K_{BT}^{α} of the ocmplex BT^+, it is also possible to introduce the constant of the heterogeneous or surface dissociation $K_{BT}^{\alpha/\beta}$ referring to a process in which the complexone T and the complex BT^+ are in the phase α while the ion B^+ is in the phase β. This constant is defined by the equation

$$RT \ln K_{BT}^{\alpha/\beta} = \mu_{BT+}^{0,\alpha} - \mu_{T}^{0,\alpha} - \mu_{B+}^{0,\beta}. \quad (24)$$

There is a simple relation between the two dissociation constants introduced and the partition coefficient of the ion B^+:

$$K_{BT}^{\alpha/\beta} = K_{BT+}^{\alpha}/P_{B+}^{\alpha\beta}. \quad (25)$$

The equation for the heterogeneous dissociation equilibrium is

$$c_{T}^{\alpha} c_{B}^{\beta} = K_{BT+}^{\alpha/\beta} c_{BT}^{\alpha} \exp(F\Delta_{\beta}^{\alpha}\varphi/RT). \quad (26)$$

The case where the complex BT^+ is very stable (i.e. its homogeneous dissociation constant K_{BT}^{α} is small) while the ion B^+ is only slightly soluble in the α-phase (the partition coefficient $P_{B+}^{\alpha/\beta}$ is small) is of special interest. One can then assume that, apart from the charged complex BT^+, the α-phase contains only one charged species—the counterion A^-. Using the usual procedures, it is possible to find the interphase potential difference for this case:[26]

$$\Delta_{\beta}^{\alpha}\varphi = \frac{RT}{F} \ln \left[\left\{ \left(\frac{c_{B+}^{\beta}}{2K_{B+}^{\alpha/\beta}} \right)^2 + \frac{c_{kom}^{\alpha}}{P_{A-}^{\alpha/\beta} K_{BT+}^{\alpha/\beta}} \right\}^{1/2} - \frac{c_{B+}^{\beta}}{2K_{BT+}^{\alpha/\beta}} \right]. \quad (27)$$

where c_{com}^{α} denotes the overall concentration of the complexone in the free and bound forms in the phase α and the activity coefficients are assumed to be unity for the sake of simplicity.

We shall consider two limiting cases arising from Eqn.(27). Supposing that the concentration of the A^-B^+ electrolyte is low. Then, by expanding Eqn.(27) as a series, we obtain

$$\Delta_{\beta}^{\alpha}\varphi \simeq \frac{RT}{2F} \ln \frac{c_{com}^{\alpha}}{P_{A-}^{\alpha/\beta} K_{BT+}^{\alpha/\beta}}. \quad (28)$$

Eqn.(28) can be given a more usual form by introducing the interphase partition coefficient of the ion B^+ taking into account complex formation:

$$\tilde{P}_{B+}^{\alpha/\beta} = c_{com}^{\alpha}/K_{BT+}^{\alpha/\beta}. \quad (29)$$

The expression for the interfacial potential is then

$$\Delta_{\beta}^{\alpha}\varphi = \frac{RT}{2F} \ln \frac{\tilde{P}_{B+}^{\alpha/\beta}}{P_{A-}^{\alpha/\beta}}. \quad (30)$$

This is a typical expression for the distribution potential which does not include directly the complexone concentration and the form of the relation is determined by the valences of the electrolyte. Eqn.(30) is valid for a 1:1 electrolyte. For arbitrary valences, it assumes the following form:

$$\frac{F}{RT}\Delta_{\beta}^{\alpha}\varphi = \frac{1}{z_B - z_A} \ln \frac{c_{com}^{\alpha}}{P_{A}^{\alpha/\beta} K_{BT}^{\alpha/\beta}}. \quad (31)$$

The dependence of $F\Delta_{\beta}^{\alpha}\varphi/RT$ on $\ln c_{com}^{\alpha}$ is described by a straight line whose slope is 1/2 for a 1:1 electrolyte, 1/3 for a 1:2 electrolyte, and 1/4 for a 2:2 electrolyte.[26]

We shall now proceed to another limiting case. Suppose that the electrolyte concentration is high so that the concentration of the complexone in the phase α is close to saturation. We then obtain for Eqn.(29)

$$\Delta_{\beta}^{\alpha}\varphi = \frac{RT}{F} \ln \frac{c_{com}^{\alpha}}{P_{A-}^{\alpha/\beta} c_{A-}^{\beta}}. \quad (32)$$

Fig.3 illustrates the dependence of $F\Delta_{\alpha}^{\beta}\varphi/RT$ on $\ln c_{A-}^{\beta}$, which consists of two linear sections. The slope of the second section is −1 for a univalent anion A^- or $1/z_{A-}$ in the arbitrary case. The point of intersection M (Fig.3) of the two sections yields $0.5 \ln (c_{com}^{\alpha} K_{BT+}^{\alpha/\beta}/P_{A-}^{\alpha/\beta})$, which makes it possible to determine the heterogeneous dissociation constant of the complex BT^+.

6. The Donnan Potential

The Donnan potential is the name given to the interphase potential difference when some of the ions cannot cross the interface between two immiscible electrolyte solutions while the remaining ions are free to move reversibly from one phase to the other. Suppose, for example, that an ion R with a charge number z_R has

such a high partition coefficient $P_R^{\alpha/\beta}$ that it is almost totally concentrated in the phase α. Apart from the ions R, the system contains a binary electrolyte B^+A^- whose concentration in the β-phase is c_{BA}^{β}

$$\alpha, R^{z_R}, B^+A^- \mid B^+A^-, \beta. \tag{33}$$

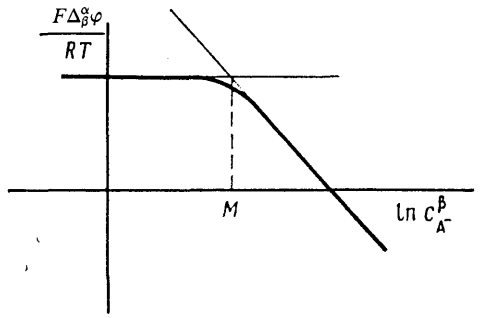


Figure 3. Dependence of the distribution potential on the electrolyte concentration in the phase β during the complex formation reaction in the phase α.

This type of equilibrium was first considered by Donnan[9] for two ideal aqueous ($\alpha \equiv \beta$) electrolyte solutions separated by a semipermeable membrane. The Donnan equilibrium was then investigated also by other workers, but the modifications which they introduced reduced in essence to the replacement in the Donnan equation of the concentrations of ions by their activities, which made it possible to change over from ideal to real solutions. Almost all investigators considered the Donnan equilibrium between two aqueous solutions. However, in the general case the phases α and β can be different and the above equilibrium can be achieved also in the absence of a semipermeable membrane.

The Donnan equilibrium at the interface between two immiscible liquids was first considered in a monograph[1] and then in another study for two ideal electrolyte solutions. Since there are inaccuracies in the study of Joos et al.,[7] we shall present the correct derivation of the Donnan equations for ideal and real immiscible electrolyte solutions in accordance with the study of Markin and Volkov.[26]

By definition, the partition coefficient of the salt is given by

$$P_{AB}^{\alpha/\beta} = a_{AB}^{\alpha}/a_{AB}^{\beta}. \tag{34}$$

Hence follows the equation relating the activities of the ion B^+ and A^- in both phases:

$$a_{B^+}^{\alpha}a_{A^-}^{\alpha} = (P_{AB}^{\alpha/\beta})^2\, a_{A^-}^{\beta}a_{B^+}^{\beta}. \tag{35}$$

From this equation and the two phase electroneutrality conditions

$$z_R c_R^{\alpha} + c_{B^+}^{\alpha} - c_{A^-}^{\alpha} = 0, \tag{36}$$

$$c_B^{\beta} - c_A^{\beta} = 0, \tag{37}$$

it is easy to find the Donnan potential:

$$\Delta_\beta^\alpha\varphi = \frac{RT}{2F}\ln\left(\frac{P_{B^+}^{\alpha/\beta}}{P_{A^-}^{\alpha/\beta}} \times \frac{\gamma_{B^+}^{\beta}\gamma_{A^-}^{\alpha}}{\gamma_{A^-}^{\beta}\gamma_{B^+}^{\alpha}}\right) + \frac{RT}{2F}\ln\left(1 + \frac{z_R^{\alpha}c_R^{\alpha}}{c_{B^+}^{\alpha}}\right). \tag{38}$$

Eqn.(38) resembles Eqn.(14) obtained by Grundwald et al.[28] but differs from it by the distribution potential of the salt defined by the first term on the right-hand side of Eqn.(38).

The Donnan potential can also be formulated as a function of the concentration of the dissolved electrolyte AB:

$$\Delta_\beta^\alpha\varphi = \frac{RT}{2F}\ln\left(\frac{P_{B^+}^{\alpha/\beta}}{P_{A^-}^{\alpha/\beta}}\frac{\gamma_{B^+}^{\beta}\gamma_{A^-}^{\alpha}}{\gamma_{A^-}^{\beta}\gamma_{B^+}^{\alpha}}\right) + \\ + \frac{RT}{F}\ln\left\{\left[1 + \left(\frac{z_R c_R^{\alpha}\gamma_{BA}^{\alpha}}{2P_{BA}^{\alpha/\beta}a_{BA}^{\beta}}\right)^2\right]^{1/2} + \frac{z_R c_R^{\alpha}\gamma_{BA}^{\alpha}}{2P_{BA}^{\alpha/\beta}a_{BA}^{\beta}}\right\}. \tag{39}$$

As can be seen from Eqns.(38) and (39), the Donnan potential is represented by a sum which includes the distribution potential and a term depending on the concentration of the ion R which does not permeate into the electrolyte. If the concentration of the ion R is low, then the second term can be assumed equal to zero and Eqns.(38) and (39) become identical with the expression for the distribution potential. The distribution of ions between phases is then determined by known expressions.

At a high concentration of the ion R, a different expression is obtained for the potential. If we put $z_R > 0$ to make the treatment concrete, we obtain

$$\Delta_\beta^\alpha\varphi = \frac{RT}{F}\ln\frac{z_R c_R^{\alpha}\gamma_{A^-}^{\alpha}}{P_{A^-}^{\alpha/\beta}a_{A^-}^{\beta}}. \tag{40}$$

In this case, the concentration of the counterions A^- in the phase α ceases to depend on the distribution coefficient and the interphase potential and approaches the limiting value

$$c_A^{\alpha} \simeq z_R c_R^{\alpha}. \tag{41}$$

The coions B^+ are then almost fully displaced from the phase α:

$$c_{B^+}^{\alpha} = \frac{1}{z_R c_R^{\alpha}}\left(\frac{P_{BA}^{\alpha/\beta}a_{BA}^{\beta}}{\gamma_{BA}^{\alpha}}\right)^2. \tag{42}$$

7. The Nernst Potential

We shall consider the especially important special case of the Donnan potential when ions of only one type can cross the boundary. Suppose that these are the B^{z_B} ions. The type and number of other ions do not play a significant role. The interphase potential difference arising in such a system is referred to as the Nernst potential:

$$\Delta_\beta^\alpha\varphi = \Delta_\beta^\alpha\varphi_B^0 + (RT/z_BF)\ln(a_B^{\beta}/a_B^{\alpha}). \tag{43}$$

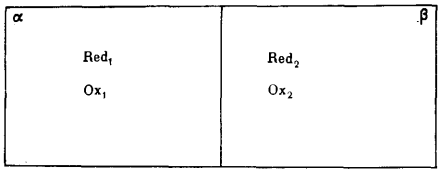
If the phases α and β are identical but are separated by a membrane permeable to the ions B^+, then $\Delta_\beta^\alpha\varphi_B^0 = 0$ and the potential difference is given by

$$\Delta_\beta^\alpha\varphi = (RT/z_BF)\ln(a_B^{\beta}/a_B^{\alpha}). \tag{44}$$

Sometimes the potential difference determined from Eqn.(43) is also referred to as the Nernst–Donnan potential, because, although historically a formula of this type was first obtained by Nernst,[27] it corresponds to a special case of the Donnan equilibrium.

8. The Oxidation-Reduction Interphase Potential

Suppose that each of the two phases, α and β, contains its own oxidation-reduction couple Red/Ox:



As a result of the exchange of n electrons across the interface, an oxidation-reduction reaction takes place:

$$\nu_1 \mathrm{Red}_1 + \nu_2 \mathrm{Ox}_2 \rightleftarrows \nu_3 \mathrm{Red}_2 + \nu_4 \mathrm{Ox}_1. \tag{45}$$

At equilibrium, the followig equality holds:

$$\nu_1 \bar{\mu}^{\alpha}_{\mathrm{Red}_1} + \nu_2 \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \nu_3 \bar{\mu}^{\beta}_{\mathrm{Red}_2} + \nu_4 \bar{\mu}^{2}_{\mathrm{Ox}_1}. \tag{46}$$

Hence we find the interphase oxidation-reduction potential:

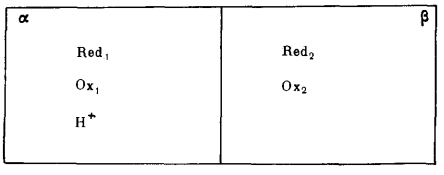
$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} + \frac{RT}{nF} \ln \frac{(a^{\alpha}_{\mathrm{Red}_1})^{\nu_1} (a^{\beta}_{\mathrm{Ox}_2})^{\nu_2}}{(a^{\alpha}_{\mathrm{Ox}_1})^{\nu_4} (a^{\beta}_{\mathrm{Red}_2})^{\nu_3}}. \tag{47}$$

In this case $\Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}}$ denotes the standard interphase oxidation-reduction potential of reaction (45):

$$\Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} = (\nu_1 \mu^{0,\alpha}_{\mathrm{Red}_1} + \nu_2 \mu^{0,\beta}_{\mathrm{Ox}_2} - \nu_3 \mu^{0,\alpha}_{\mathrm{Ox}_1} - \nu_4 \mu^{0,\beta}_{\mathrm{Red}_2})/nF, \tag{48}$$

where n is the number of electrons transferred from Red_1 to Ox_2. In terms of its physical significance, Eqn.(48) represents the interphase potential for equal activities of the ions of the oxidised and reduced forms in each solvent. We may note that the interphase oxidation-reduction potential is defined by Eqns.(47)–(48) when reaction (45) occurs even when the oxidant or reductant in any of the redox pairs is a neutral species.

If reaction (45) is accompanied by a change in the pH in one of the phases, i.e.



and the reaction

$$\nu_1 \mathrm{Red}_1 + \nu_2 \mathrm{Ox}_2 \rightleftarrows \nu_3 \mathrm{Red}_2 + \nu_4 \mathrm{Ox}_1 + m\,\mathrm{H}^{+}_{\alpha}, \tag{49}$$

takes place, then from the condition for equilibrium

$$\nu_1 \bar{\mu}^{\alpha}_{\mathrm{Red}_1} + \nu_2 \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \nu_3 \bar{\mu}^{\beta}_{\mathrm{Red}_2} + \nu_4 \bar{\mu}^{\alpha}_{\mathrm{Ox}_1} + m \bar{\mu}^{\alpha}_{\mathrm{H}^+} \tag{50}$$

it is possible to find the interphase redox potential

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} + \frac{RT}{nF} \ln \frac{(a^{\alpha}_{\mathrm{Red}_1})^{\nu_1} (a^{\beta}_{\mathrm{Ox}_2})^{\nu_2}}{(a^{\alpha}_{\mathrm{Ox}_1})^{\nu_4} (a^{\beta}_{\mathrm{Red}_2})^{\nu_3} (a^{\alpha}_{\mathrm{H}^+})^{m}}, \tag{51}$$

where

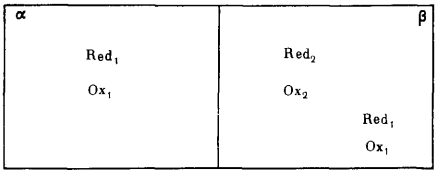
$$\Delta^{\alpha}_{\beta}\varphi = (\nu_1 \mu^{0,\alpha}_{\mathrm{Red}_1} + \nu_2 \mu^{0,\beta}_{\mathrm{Ox}_2} - \nu_3 \mu^{0,\alpha}_{\mathrm{Ox}_1} - \nu_4 \mu^{0,\beta}_{\mathrm{Red}_2} - m\mu^{0,\alpha}_{\mathrm{H}^+})/nF. \tag{52}$$

Analysis of the influence of the interface between two liquids on the standard redox potential of an electron-exchange reaction[11-14] has shown that, by selecting the phases α and β, it is possible to displace the standard chemical potential of the oxidants and reductants in the required direction and to achieve at the interface reactions which do not occur at a sufficiently high rate in each phase.

9. The Mixed Potential

If the two immiscible liquids each contain, apart from their own redox couple also common ions or compound redox couples, then a mixed potential is established at the interface to which both the interphase oxidation-reduction potential and the distribution of the ions between the phases contribute.

There is a possibility of various combinations of electron-exchange reactions in the two-phase system. Suppose, for example, that each of the phases α and β has its own redox couple but one of the couples is soluble in both phases:



In this case electron-exchange reactions are possible both at the interface, i.e.

$$\mathrm{Red}^{\alpha}_1 + \mathrm{Ox}^{\beta}_2 \rightleftarrows \mathrm{Ox}^{\alpha}_1 + \mathrm{Red}^{\beta}_2, \tag{53}$$

and in the bulk of the phase β:

$$\mathrm{Red}^{\beta}_1 + \mathrm{Ox}^{\beta}_2 \rightleftarrows \mathrm{Ox}^{\beta}_1 + \mathrm{Red}^{\beta}_2. \tag{54}$$

It follows from the condition for equilibrium that

$$\bar{\mu}^{\beta}_{\mathrm{Red}_1} - \mu^{\alpha}_{\mathrm{Red}_1} = 0, \tag{55}$$

$$\bar{\mu}^{\beta}_{\mathrm{Ox}_1} - \bar{\mu}^{\alpha}_{\mathrm{Ox}_1} = 0, \tag{56}$$

whence

$$\Delta^{\alpha}_{\beta}\varphi = \frac{RT}{nF} \ln \frac{P^{\alpha/\beta}_{\mathrm{Ox}_1}}{P^{\alpha/\beta}_{\mathrm{Red}_1}} + \frac{RT}{nF} \ln \frac{a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1}}{a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1}}. \tag{57}$$

The standard potential for reaction (53) is defined by the expression

$$\Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} = (RT/nF) \ln (P^{\alpha/\beta}_{\mathrm{Ox}_1}/P^{\alpha/\beta}_{\mathrm{Red}_1}). \tag{58}$$

Eqn.(57) is identical with Eqn.(14) for the partition potential only in the case of a two-electron reaction subject to the condition that $z_{\mathrm{Red}_1} = -1$, $z_{\mathrm{Ox}_1} = +1$, and $a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1} / a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1} = 1$. The last requirement, concerning the ratio of the concentrations of the redox couple, is artificial in character and may hold only at one point for definite fixed activites of all the ingredients. It does not follow from the phase electroneutrality condition because, apart from the redox couples, there are also other ions in both phases.

Eqn.(57) does not include the second redox couple $\mathrm{Red}_2/\mathrm{Ox}_2$ but the latter does enter implicitly into the second term on the right-hand side of this equation. The second redox couple is forced to become automatically adjusted with respect to the first because, apart from Eqns.(55) and (56), a further two equations, determined by the equilibrium in the system, also hold:

$$\bar{\mu}^{\alpha}_{\mathrm{Red}_1} + \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \bar{\mu}^{\alpha}_{\mathrm{Ox}_1} + \bar{\mu}^{\alpha}_{\mathrm{Red}_2}, \tag{59}$$

$$\bar{\mu}^{\beta}_{\mathrm{Red}_1} + \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \bar{\mu}^{\beta}_{\mathrm{Ox}_1} + \bar{\mu}^{\beta}_{\mathrm{Red}_2}. \tag{60}$$

The introduction of a common electrolyte $B_p A_t$ into both phases is not reflected in the form of Eqn.(57) but, by virtue of the electroneutrality of both phases, i.e.

$$\sum_i z_i^{\alpha} c_i^{\alpha} = 0, \quad \sum_j z_j^{\beta} c_j^{\beta} = 0$$

the distribution of the concentrations of the redox components in each phase changes, which makes a considerable contribution to the second term on the right-hand side of Eqn.(57).

The majority of the redox reactions occurring on the liquid water–oil and water–biomembrane interfaces are accompanied by changes in pH, for example:

$$\mathrm{NADH} \rightleftarrows \mathrm{NAD}^+ + 2e^- + \mathrm{H}^+. \tag{61}$$

We shall consider a system of two immiscible liquids α and β:

α	β
Red_1	Red_2
Ox_1	Ox_2
	H^+
	Red_1
	Ox_1

Suppose that each phase has its own redox couple and that one of them is common to both phases:

$$\mathrm{Red}_1^{\alpha} + \mathrm{Ox}_2^{\beta} \rightleftarrows \mathrm{Ox}_1^{\alpha} + \mathrm{Red}_2^{\beta} + m\mathrm{H}^+_{\beta},$$

$$\mathrm{Red}_1^{\beta} + \mathrm{Ox}_2^{\beta} \rightleftarrows \mathrm{Ox}_1^{\alpha} + \mathrm{Red}_2^{\beta} + m\mathrm{H}^+_{\beta}, \tag{62}$$

If n electrons are transferred from Red_1 to Ox_2 in the course of the reactions then, when $m \neq n$, we obtain from the equilibrium condition an expression for the mixed potential:

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} - \frac{RT}{(n-m)F} \ln \frac{a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1}}{a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1}}, \tag{63}$$

in which the standard potential is defined by the formula

$$\Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} = \frac{RT}{(n-m)F} \ln \frac{P^{\alpha/\beta}_{\mathrm{Ox}_1}}{P^{\alpha/\beta}_{\mathrm{Red}_1}}. \tag{64}$$

From the condition for thermodynamic equilibrium and the electroneutrality of phases for reaction (61), one can write $4+2=6$ equations for the two redox couples, which exceeds the number of independent variables in the system. If a proton equilibrium is established during reaction (61) between the phases α and β, then the mixed potential can be formulated as follows:[26]

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} - \frac{RT}{nF} \ln \frac{a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1}}{a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1}} + \frac{2{,}3RT}{nF} \Delta^{\alpha}_{\beta}\mathrm{pH}, \tag{65}$$

where

$$\Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} = -\frac{RT}{nF} \ln \frac{P^{\alpha/\beta}_{\mathrm{Red}_1}}{P^{\alpha/\beta}_{\mathrm{Ox}_1} P^{\alpha/\beta}_{\mathrm{H}^+}}. \tag{66}$$

IV. MEASUREMENTS OF INTERPHASE POTENTIAL JUMPS

1. The Tetraphenylborate Hypothesis

It is known from thermodynamics that the absolute difference between electrical potentials can be measured only in conductors of identical composition. For this reason, the difference between the Galvani potentials between a point in an aqueous phase and a point in the bulk of an organic solvent is not susceptible to experimental measurement.

For the determination of the difference between Galvani potentials and surface potential jumps, it is necessary to resort to additional non-thermodynamic hypotheses. It is comparatively easy to measure the relative change in the phase boundary potential difference when the type of dissolved salt is altered, for example, when one of the ions in the salt is changed. One can then measure the partition coefficient of each salt $P^{\alpha/\beta}_{\mathrm{salt}}$. With the aid of Eqn.(5), the phase boundary potential can be expressed in the form

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi_i - \frac{RT}{z_i F} \ln P^{\alpha/\beta}_{\mathrm{salt}} \tag{67}$$

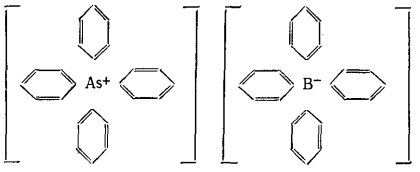
Thus it is possible to set up a scale of the changes in the potentials when one of the ions is altered, but this scale will include the unknown constant term $\Delta^{\alpha}_{\beta}\varphi^0_i$—the standard partition coefficient of the unchanged ion. The problem reduces to the correct selection of the zero on this scale.

The zero cannot be chosen by thermodynamic methods and requires the invocation of additional hypotheses. The most popular tetraphenylborate hypothesis was formulated in 1960 [28] and then developed in other studies.[29–42] The history of its development has been described in a review.[43]

The essential feature of the tetraphenylborate hypothesis is as follows. If one selects a cation and an anion with identical standard energies of transfer between two solvents, then the interphase distribution potential for such a salt is found to be zero. In this case the partition coefficients of the ions are equal to the partition coefficient of a salt, which can be readily determined experimentally. Having determined it, we find the standard free energy of the transfer and the standard distribution potentials of the individual ions. As can be readily seen, these potentials are identical in absolute magnitude and opposite in sign:

$$\Delta^{\alpha}_{\beta}\varphi^0_{+} = -\Delta^{\alpha}_{\beta}\varphi^0_{-}. \tag{68}$$

It now remains only to select the suitable ions. Preference has been given to different ions in different investigations. For example, Koczorowski[3] used tetraethylammonium picrate $(Et)_4NPi$. In other studies[28–43], preference was given to tetraphenylarsonium tetraphenylborate (TPATPB). The constituent ions of this salt TPB^- and TPA^+, i.e.



are similar, firstly, because they are symmetrical species whose shapes approach those of spheres having identical and fairly large radii, which permits the assumption that the hydrophobic effect is the same for both and, secondly, their charges are equal in absolute magnitude and are located in centres of ionic spheres and are shielded from the solvent, so that the electrostatic contribution to the free energy of transolvation of these ions should be the same. The ions have a comparatively low polarisability and a low surface charge density and hardly enter into specific interactions with the solvent molecules. All these factors permit the hope that the standard energies of the transfer of such ions will be the same for any pair of solvents.

With the aid of the tetraphenylborate hypothesis, it is possible to determine the standard distribution potentials by methods such as cyclic voltammetry, chronopotentiometry, polarography at a dropping electrolyte electrode, chronoammetry, and also solubility and extraction data.[31,35,37,38,40–42,44,45]

Fig.4 illustrates a typical cyclic voltammogram obtained at a scanning rate of 25 mV s^{-1} in the water–nitrobenzene (NB) system containing 10 mM TPATPB in the non-aqueous phase and 10 mM Li_2SO_4 in water.[53] The range of applied potential differences is limited in the negative region by the potential of the transfer of TPA^+ from nitrobenzene to water and in the positive region by the potential of the transfer of TPB^-. Since

$$\Delta^{H_2O}_{NB}\varphi^0_{TPB^-} = -\Delta^{H_2O}_{NB}\varphi^0_{TPA^+},$$

it is possible to select the starting point for the readings on the potential scale and to change over, as in Fig.4, from the applied potential difference scale to the Galvani potential scale or the distribution potential scale.

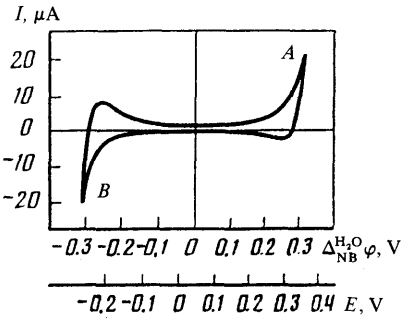


Figure 4. Cyclic voltammetric curve for the water–nitrobenzene system in the presence of TPATPB in nitrobenzene and of Li_2SO_4 in water. Peaks *A* and *B* are due to the transfer of TPA^+ and TPB^- from nitrobenzene to water respectively. The experimental curve has been taken from Hundhammer and Solomon.[31]

The block diagram of the apparatus, on which it is possible to determine the distribution potentials of ions and to investigate the electrochemical properties of the interface between two immiscible

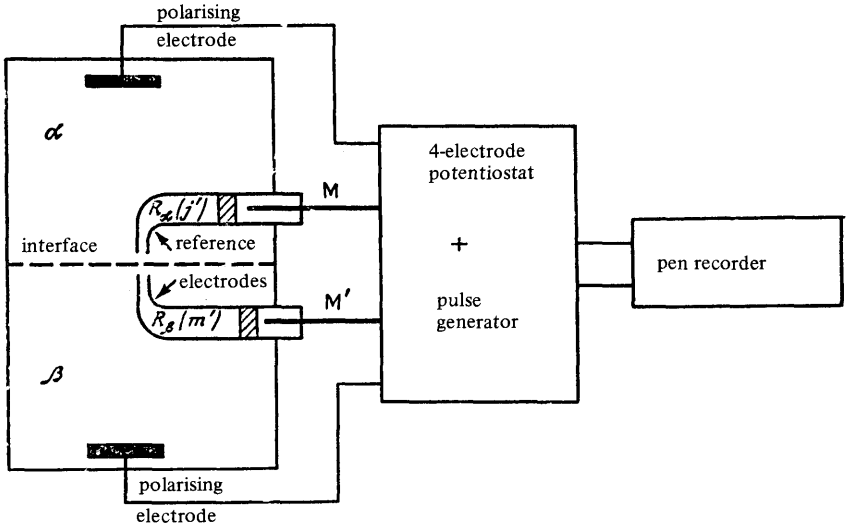


Figure 5. Diagram of the four-electrode apparatus for the measurement of the electrochemical characteristics of the interface between two immiscible electrolyte solutions.

liquids, is illustrated in Fig.5 and the cell and the electrical circuit are presented in Fig.6. The standard distribution potential of an ion depends both on the nature of the solvent (primarily on the optical and static dielectric constant) and on the ionic radius.

Fig.7 presents the dependence of the distribution potentials of ions on their radii for the water–nitrobenzene, water–1,2-dichloroethane, and water–dichloromethane systems plotted on the basis of a series of data[35,37,38,40–42,44–54] and published in a review.[56] The radii of inorganic ions were taken from Gourary and Adrian[57] and those of tetra-alkylammonium salts were taken from Robinson and Stokes.[58]

Figs.7 and 8 show that the distribution potential of an ion decreases sharply with increase in the size of the ion and in the dielectric constant of the non-aqueous solvent. The continuous line in Figs.7*a* and 7*b* represents the theoretical calculation with the aid of non-local electrostatic theory.[13,14] For ions with radii less than 0.3 nm, the main contribution to $\Delta_{\beta}^{\alpha}\varphi_i^0$ comes from the electrostatic component of the free energy of transolvation, while for ions with a radius greater than 0.3 nm the contribution of the solvophobic effect is greatest.[13,14]

2. Methods for the Measurement of the Interphase Potential Difference

The difference between the Volta potentials and the change in the surface or Galvanic potential in a system of two immiscible electrolyte solutions can be measured by the dynamic condenser, radioactive probe, and streaming electrode methods and also with the aid of concentration cells.

The dynamic condenser method, proposed by Kelvin, was subsequently developed in detail in other studies.[59,60] All the experimental methods for the measurement of Volta potentials between the phases α and β are based on the compensation method, which involves the application of a potential difference equal in absolute magnitude but opposite in sign to the Volta potential between the phases α and β.[59–86]

Two types of sensors are normally employed for the periodic measurement of the capacitance of the condenser formed by the surface of the electrode and the interface investigated, namely vibrating and rotating electrodes. The vibrating electrode is less complex than the rotating electrode but its stability is lower.

The block diagram of the apparatus for the measurement of the Volta potential by the dynamic condenser method is presented in Fig.9.[61] The generator of mechanical vibrations causes the vibration of a gold electrode placed at a distance of 0.2–1.0 mm from the surface of the liquid phase investigated. The aqueous solution is connected via a salt bridge filled with a saturated KCl solution (to eliminate the diffusion potential) to a reversible reference electrode. The displacement current arising in the vibration of the gold electrode is compensated by applying to the vibrating electrode a potential equal in magnitude but opposite in sign to the measured Volta potential. The equivalent electrical circuit for the method[62] is presented in Fig.10.

The Volta potential $\Delta\psi$ at the boundary between two immiscible equilibrated (mutually saturated) solutions of electrolytes B^+A^- can be determined experimentally as the compensation potential E_1 in the cell

$$\begin{matrix} M\,|\text{water},\, B^+A^-|\text{gas}|\text{Nitrobenzene},|M. \\ \qquad\qquad\quad B^+A^- \end{matrix} \qquad (I)$$

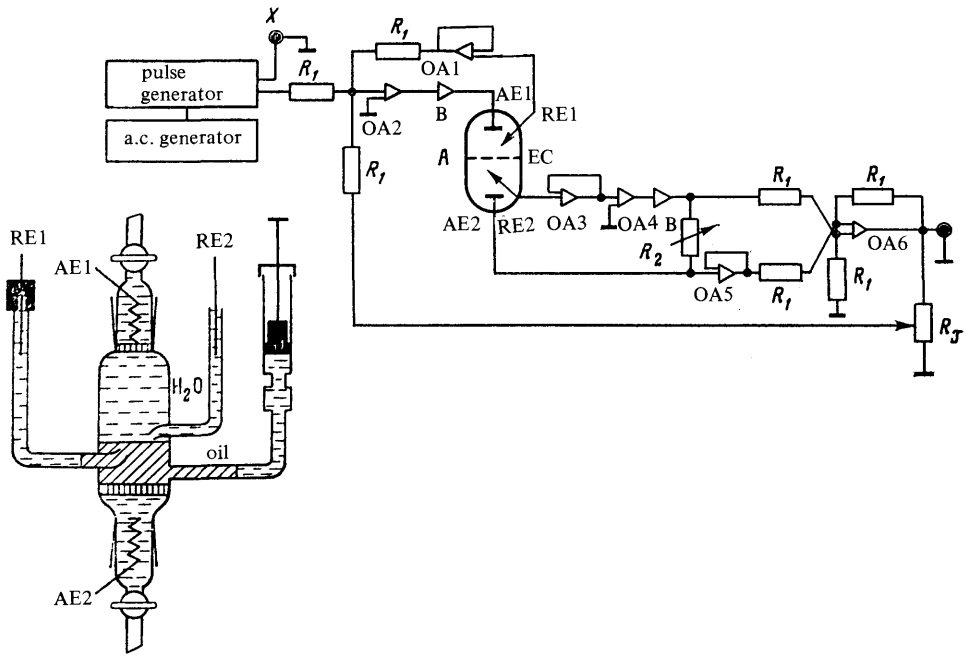


Figure 6. The cell and the electrical circuit of the apparatus for the measurement of the electrochemical properties of the interface between two immiscible electrolyte solutions; EC—electrochemical cell; OA—operational amplifier; AE—auxiliary electrode; RE—reference electrode; A—oil–water interface.[46]

The term gas implies a chemically inert gas phase, i.e. nitrogen, argon, or pure air, M is a metallic electrode, and B^+A^- is the electrolyte.

The Volta potential can be measured by the vibrating electrode method as the difference between the e.m.f.'s E_{II} and E_{III} of cells (II) and (III):

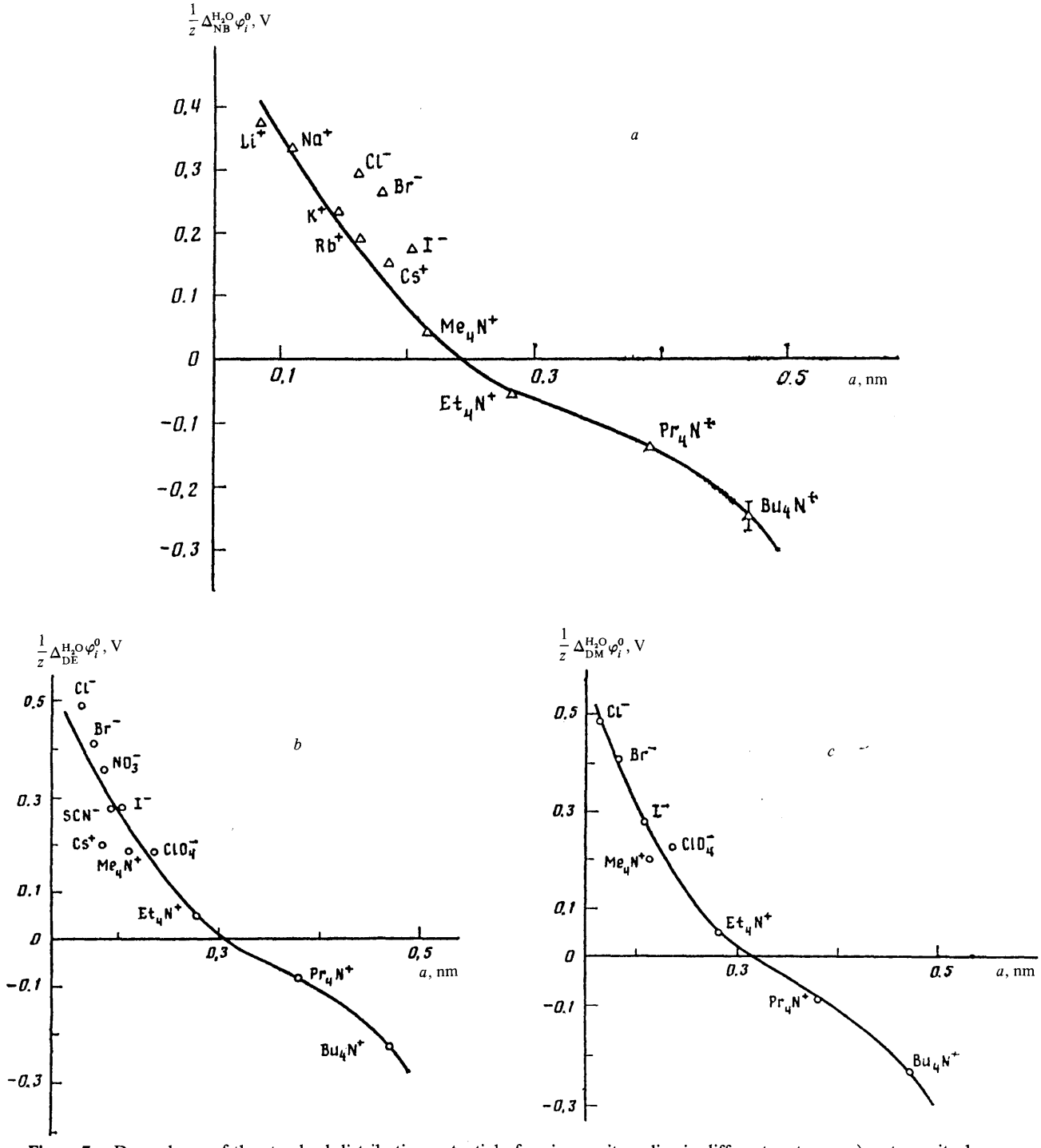


Figure 7. Dependence of the standard distribution potential of an ion on its radius in different systems: *a*) water–nitrobenzene; *b*) water–1,2-dichloroethane (DE); *c*) water–dichloromethane (DM). The experimental data have been taken from a review.[56]

$$M\,|\,\text{vibrating electrode}\,|\,N_2\,|\,\text{nitrobenzene } B^+A^-\,|\,\text{water, } B^+A^-\,|\,\text{saturated calomel electrode}\,|\,M, \quad \text{(II)}$$

$$M\,|\,\text{vibrating electrode}\,|\,N_2\,|\,\text{water, } B^+A^-\,|\,\text{saturated calomel electrode}\,|\,M. \quad \text{(III)}$$

In other words, the relation

$$\Delta^{H_2O}_{org}\psi(MX) = E_I = E_{II} - E_{III}, \quad (69)$$

holds, provided that the following conditions are fulfilled: (a) the constancy of the surface potential of the vibrating electrode: (b) the constancy of the surface potential of the water-saturated nitrobenzene phase; (c) the constancy of the surface potential of the nitrobenzene-saturated aqueous phase; (d) the stability of the calomel electrode and a constant and identical contribution of the diffusion potential between the aqueous phase and the solution in the calomel electrode.

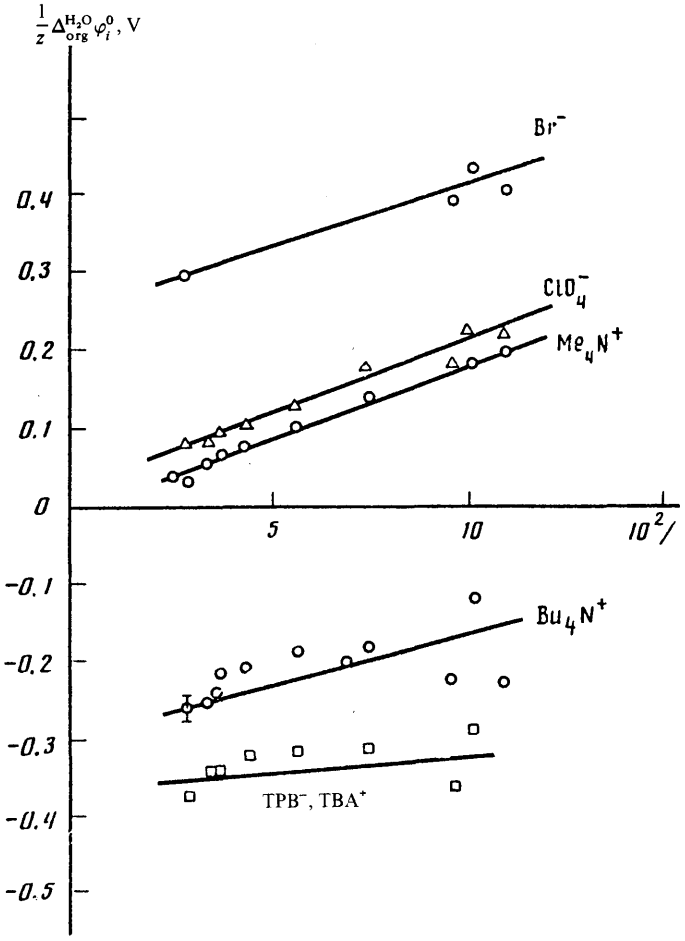


Figure 8. Dependence of the standard distribution potential of the ion on the static dielectric constant ε of the non-aqueous solvent. The experimental data were taken from a review.[56]

The design of the rotating electrode has been described by Dudko[64] and by Freyer and Ohlenbusch.[65] The equivalent circuit is presented in Fig.11. The rotating electrode is placed over a circular cell in such a way that the geometrical centre of the circle which it describes during its rotation coincides with the geometrical centre of the cell. The cell, divided by a partition into identical sections, is filled with the test liquids.

The essential feature of the radioactive probe method is the reduction of the resistance of the air gap between the electrode and the surface of the test liquid when it is bombarded with α-particles from a radioactive source.[66,67] As a result of ionisation, the gap becomes electrically conducting due to the appearance of charged particles. The ^{210}Po, ^{241}Am, and ^{239}Pu isotopes are normally employed.[68,72,73] The ^{241}Am isotope has an advantage over ^{210}Po because of its longer half-life (458 years instead of 138.4 hours); furthermore, ^{241}Am can be used in the form of a foil which has a large surface area and can readily be insulated.[73] The accuracy and reproducibility of the results in the radioactive probe method is lower than in the vibrating electrode method. The equivalent circuit of the method is presented in Fig.12.

An obligatory condition in the measurement of the Volta potential by the radioactive probe method is careful shielding of the measuring chamber and of the electrometer input. An unduly large gap between the electrode and the surface of the solution of the test electrolyte is frequently a source of errors in the measurement of the potential difference as a result of scattering of the radiation and parasitic leakages. If the gap is too small, incorrect values are also obtained owing to the interaction of α-particles with the molecules of the test liquid. The design of the apparatuses whose operation is based on the radioactive probe method and the experimental technique have been described in detail.[69]

In the streaming electrode method,[70,71] a stream of the test liquid flows downwards along the axis of a tube whose inner surface is coated with a down-flowing film of another liquid (Fig.13). The reversible reference electrodes placed in the solutions are connected to the measuring system consisting of a potentiometer and a null instrument with a very large internal resistance. At the instant of compensation, the external potential of this stream is equal to the external potential of the solution flowing along the inner walls of the cylinder. This method is rarely used to investigate the interface between two immiscible electrolyte solutions.[71,73]

All three methods yield identical results in the determination of the Volta potentials of electrolyte solutions.[74-76]

3. The Adsorption Potential

The term adsorption potential is given to the interphase difference between Galvani potentials due to the adsorption of ions or dipoles at the interface.

The problem of the appearance of the adsorption potential, despite its apparent simplicity, has been the subject of a prolonged controversy.[2,4,25,80-86] If two immiscible liquids, α and β, are in equilibrium, the interphase potential difference arises in a transition adsorption layer between them. Formally, it is possible to calculate the electrolyte distribution potential knowning only the solvation energies of the ions in each phase without paying attention to the properties of the interfacial adsorption layer. However, at equilibrium, the properties of the ions in the adsorption layer are unambiguously related to the properties of the ions in the bulk of each of the

phases in contact. The distribution potentials can therefore be calculated in two ways—from the bulk-phase properties of the solvents α and β and from the properties of the adsorption layer.[4]

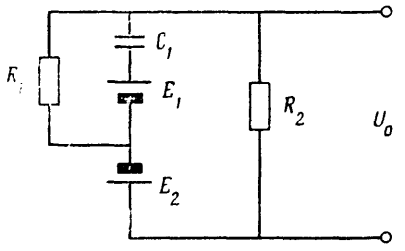


Figure 10. Equivalent electric circuit of the vibrating electrode: R_1—leakage resistance between the electrodes; C_1—capacitance of the vibrating electrode; E_1—potential difference between the vibrating electrode and the surface investigated; E_2—e.m.f. of the source of compensating potential; R_2—resistance in the compensation circuit.

At the beginning of this century, Beutner[87,88] showed that the formal thermodynamic theory of the distribution of ions is sufficient for the determination of the potential difference between two immiscible electrolyte solutions and that no additional hypotheses need be introduced into it.[87,88] However, these views have been criticised.[89,90] Some workers[89,91,92] regarded the adsorption potential as being superimposed on the partition potential jump, while others[2,4,93] assumed that the adsorption potential jump is part of the partition potential.

The partition potential is a purely thermodynamic concept. The calculation of the adsorption potential is outside the framework of thermodynamics. Definite structural ideas are used in it. Nevertheless, both approaches lead to identical results if the hypothesis concerning the structure of the adsorption layer corresponds accurately enough to the real picture. To some extent the adsorption approach appears to be more general: if ionic equilibrium at the interface has been disturbed as a result of the blocking of the interface by a surfactant or if the non-aqueous solvent is non-polar (octane, decane, and heptane), then the theory of distribution potentials cannot be applied to such systems, while adsorption analysis makes it possible to describe them with fair accuracy.[4,68,72,82]

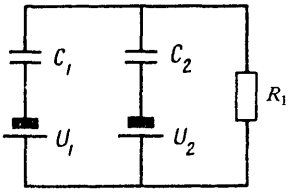


Figure 11. Equivalent electrical circuit of the rotating electrode: R_1—load resistance; C_i—capacitance between the half-cells and the rotating electrode; U_i—compensating potential.

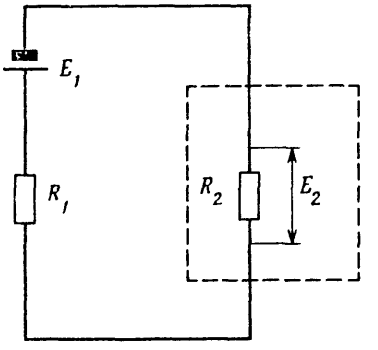


Figure 12. Equivalent circuit for the measurement of the potential jump by the radioactive probe method: E_1—measured potential difference; R_1—input resistance of the electrometer; R_2—resistance of the air gap; E_2—potential jump at the input to the electrometer.

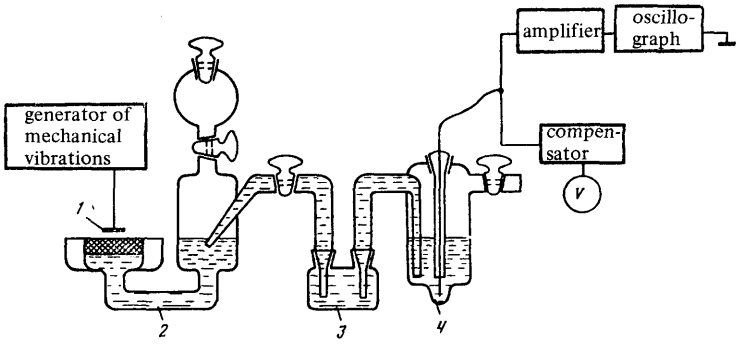


Figure 9. Block diagram of the apparatus for the measurement of the Volta potentials between two immiscible liquids: *1*) vibrating gold electrode; *2*) aqueous electrolyte solution; *3*) salt bridge for the elimination of the diffusion potential; *4*) reference electrode.[61]

V. TEST OF THE THERMODYNAMIC THEORY OF INTERPHASE POTENTIALS

The following cell has been proposed for the measurement of interfacial potentials:[25]

$$\begin{array}{l}\mathrm{Hg, Hg_2Cl_2}\,|\,\mathrm{H_2O, KCl}\,|\,\mathrm{H_2O, M^+X^-}\,|\,\text{diisopropyl ketone or nitrobenzene, } \mathrm{M^+X^-}\,|\,\text{diisopropyl ketone, } (\mathrm{Et})_4\mathrm{NPi}\,|\,\mathrm{H_2O, Et_4N^+, Pi^-}\,|\,\mathrm{Hg_2Cl_2, Hg;}\end{array} \quad \text{(IV)}$$

$$\Delta^{H_2O}_{RE_1}\varphi = \text{const}\ \Delta^{H_2O}_{H_2O}\varphi \simeq 0\ \Delta^{org}_{H_2O}\varphi_{M^+X^-}\ \Delta^{org}_{org}\varphi = \text{const}\ \Delta^{H_2O}_{org}\varphi_{Et_4NPi} = \text{const}\ \Delta^{RE_2}_{H_2O}\varphi = \text{const}$$

where M^+X^- is the salt investigated, distributed between the two solvents, the distribution corresponding to equilibrium, and RE is the reference electrode. If it is supposed that the diffusion potentials $\Delta^{H_2O}_{H_2O}\varphi$ and $\Delta^{org}_{org}\varphi$ are zero while the distribution potential $\Delta^{H_2O}_{org}\varphi_{Et_4NPi}$ = const., then, by replacing the M^+ or X^- ions by others, it is possible to determine the change in the distribution potential $\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX}$ on passing from one salt (M_1X) to the other (M_2X):

$$\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX} = \frac{RT}{F}\ln\frac{P^{org/H_2O}_{M_1X}}{P^{org/H_2O}_{M_2X}} = \frac{RT}{2F}\ln\frac{P^{org/H_2O}_{M_1}}{P^{org/H_2O}_{M_2}} \quad (70)$$

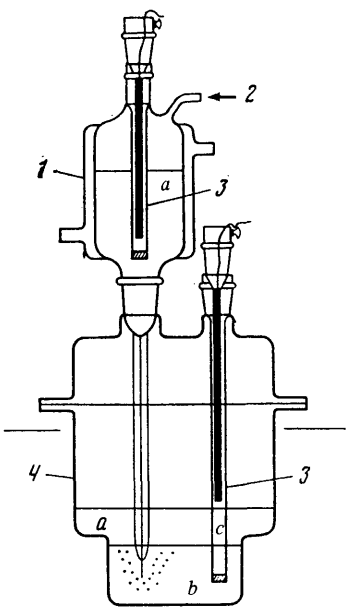


Figure 13. Diagram of apparatus for the measurement of the potential difference at the interface between two immiscible electrolyte solutions by the flow method: *a*) aqueous solution; *b*) oil; *c*) aqueous salt bridge; *1*) water reservoir; *2*) inlet for an inert gas; *3*) reference electrode; *4*) vessel for the streaming electrode.

Eqn.(70) has been tested experimentally for the water–isopropyl ketone,[25] water–acetonitrile, water–quinoline,[86] and water–nitrobenzene[68,81,85] systems.

It has also been suggested that $\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX}$ be measured in the cell[81]

$$\begin{array}{l}\text{Au, vibrating electrode}\,|\,\text{gas}\,|\,\text{nitrobenzene, } \mathrm{M^+X^-}\,|\,\text{water, } \mathrm{M^+X^-}\,|\,\text{water, sat.KCl}\,|\,\mathrm{Hg_2Cl_2, Hg;}\end{array} \quad \text{(V)}$$

$$\Delta^{gas}_{Au}\varphi = \text{const}\ \ \Delta^{org}_{gas}\chi = \text{const}\ \ \Delta^{H_2O}_{org}\varphi\ \ \Delta^{H_2O}_{H_2O}\varphi_{dif} = 0\ \ \ \Delta^{RE}_{H_2O}\varphi = \text{const.}$$

The potential measured in cell (V) is the sum of the potential jumps at all the interfaces. When M_1X is replaced by M_2X in cell (V), it is possible to obtain $\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX}$ as the difference between the potentials of cell (V) in the presence of M_1X and M_2X. The methods of measurement and calculation have been described in detail elsewhere.[81]

Table 2. The distribution potential differences for two binary electrolytes M_1/M_2 with a common ion X in the water–nitrobenzene system at 298 K.

M_1/M_2	X	$\Delta^{M_1}_{M_2}\Delta^{NB}_{H_2O}\varphi$, mV			
		from Ref.81	from Ref.25	from Ref.68	calc. by Eqn.(70)
Na^+/K^+	Cl^-, Br^-, I^-	−52	−53	—	−50
Li^+/K^+	Br^-, I^-	−78	—	—	−73
Cl^-/I^-	K^+, Na^+, Et_4N^+, But_4N^+	+98	+102	+100. +92	+95
Br^+/I^-	Li^+, Na^+, K^+, But_4N^+	+79	—	+70. +75	+77
Cl^-/NO_3^-	K^+	+70	—	—	—
Cs^+/K^+	Cl^-	+40	—	—	—
K^+/NH_4^+	I^-	+30	—	—	—
Et_4N^+/K^+	I^-, Cl^-	+128	+126	+120	+124
Me_4N^+/K^+	—	—	—	+65	—

The results of the test of the thermodynamic theory of distribution potentials are presented in Table 2, where it is evident that the experimental changes in the distribution potential of the salt following the replacement of one of the ions agree satisfactorily with the result of the calculation from the partition coefficient of the salt by Eqn.(70).

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The interest in the processes occuring at the interface between two immiscible liquids is associated with the fact that we live in essence in a multiphase world. Almost all energy-transforming processes in living systems (respiration, photosynthesis) take place at the interface between two liquid phases.

It may be hoped that the role of the boundary potentials and of the spatial charge separation on the surfaces of biomembranes and their models in bioenergetic mechanisms of respiration, artificial and natural photosynthesis, and the coupling of biochemical reactions will be elucidated in the next few years.

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Contemporary Ideas About the Conformations of Eight-membered Cyclic Systems with Planar Fragments

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The results of conformational studies on eight-membered cyclic compounds that contain from one to four planar fragments in exo- or endo-cyclic positions of the molecule have been correlated. By analysing the systematic changes in the torsion angles and folding parameters, which were selected as the main quantitative criteria of the conformational state of the class of compounds being examined, it is possible to present a sufficiently complete and consistent picture of their conformational behaviour, which has a diversity that is determined by the relative configuration and nature of both the planar fragments and the heteroatoms contained in the ring. Special consideration has been given to the basis for the NMR spectroscopic criteria used in identification of the respective conformations.
The bibliography includes 230 references.

CONTENTS

I. Introduction 1142
II. Eight-membered rings with a single planar fragment 1143
III. Derivatives of 1,2-cyclooctadienes 1144
IV. Derivatives of 1,3-cyclooctadienes 1145
V. Derivatives of 1,4-cyclooctadienes 1147
VI. Derivatives of 1,5-cyclooctadienes 1153
VII. Derivatives of cycloocta-trienes and -tetraenes 1155

I. INTRODUCTION

Molecular carbocyclic and heterocyclic systems that are made up of so-called medium rings containing from 7 to 12 atoms in the ring exhibit many specific properties in comparison with well-studied six-membered rings. During the last ten years there has been a substantial increase in the number of published works devoted to eight-membered cyclic systems, among which rings that contain a planar group of atoms with unsaturated bonds (a carbon group, double bond, aromatic ring) constitute a distinctive group of compounds. They can form the basis for the construction of a variety of systems containing from one to four planar fragments in different positions of the eight-membered ring. The design possibilities are increased with the introduction of different heteroatoms into the ring. Inorganic heterocycles made up of a combination of different heteroatoms have been synthesised as well as mixed molecular systems containing heteroatoms and organic aromatic rings (phenyl and naphthyl) as planar fragments.

The extensive synthetic possibilities have also stimulated interest in the stereochemistry of such systems. The development of conformational studies in this field has occurred irregularly. The elaboration of methods of calculation in molecular mechanics made it possible for the basic principles of the conformational analysis of cyclooctenes and cyclooctadienes to be developed as far back as 1968–1973.[1,2] However, the rules developed for carbocyclic systems did not prove to be very suitable for their heterocyclic analogues, since the points on the potential energy surface which are saddle-shaped for the former are often transformed to global minima for the latter. In order to develop the conformational analysis of heterocyclic systems as a whole, the creation of tests and quantitative criteria for the identification of possible conformers was required. Their development was completed in the 1970's mainly on six-membered rings; the progress achieved was reflected in a number of monographs and reviews.[3-7] However, they also proved inadequate for conversion to eight-membered systems because of the greater conformational mobility and flexibility of the latter and also due to the absence of quantitative selection criteria (and in a number of cases even because of the nomenclature system of the respective conformers).

The basic study of Cremer and Pople[8] concerning the quantitative representation of the conformations of cyclic compounds was published in 1975, and in 1981 these concepts were developed for eight-membered rings,[9-11] which stimulated an increase in the number of published works on eight-membered rings. At the present time it has become necessary to interpret the accumulated material on carbocycles and heterocycles within the framework of a single system of nomenclature and a single approach based on the quantitative representation of conformers.

In this review the main focus of attention has been directed to examining the conformational features of eight-membered heterocyclic compounds. We considered it practicable to introduce into the text of the review information on a number of recently synthesised compounds of this type that have not yet been studied in relation to their conformation and were not included in a recent review.[12] The most fundamental and well verified information is reported for carbocycles. The torsion angles about the cyclic bonds and the folding parameters[7,10,15] have been selected as quantitative criteria in discussing the conformational state of the molecules examined. This together with the standardised nomenclature proposed previously for cyclooctane[13,14] and used by us make it possible to build up a unified pattern of conformational behaviour of eight-membered carbocycles and heterocycles which are so diverse in the conformational sense. The basic conformations and their nomenclature for each series of compounds is given in the respective Sections. The effect of the successive introduction of one, two, three, or four planar fragments into a ring is also examined, and for two average cases the effect of the relative configuration of the planar fragments on the conformation of the compounds is also discussed.

II. EIGHT-MEMBERED RINGS WITH A SINGLE PLANAR FRAGMENT

1. General Concepts of the Conformations of Cyclooctane Systems

In examining the conformations of eight-membered rings with planar fragments we have primarily used the nomenclature systems introduced for cyclooctane itself[13,14] as a basis. An eight-membered ring can adopt ten conformations, which constitute four groups (Fig.1): (a) the boat-chair (BC) group which is simply boat-chair (BC) and skewed or twist-boat-chair (TBC); (b) the crown group which is crown, chair-chair (CC), and skewed or twist-chair-chair (TCC); (c) the boat group which is boat-boat (BB), twist-boat (TB), and boat (B); (d) the chair group which is long chair (LC) and twist-chair (TC). For each conformation, Fig.1 indicates the sequence of torsion angles in the ring (namely, the angles between the planes formed by three neighbouring atoms of the ring: angle φ_1 corresponds to the angle along the C(1)–C(2) bond between the planes containing the atoms in positions 8, 1, 2 and 1, 2, 3; angle φ_2 is the angle between the planes containing the atoms in positions 1, 2, 3 and 2, 3, 4; etc.). The line in Fig.1 corresponds to the symmetry element (axis or plane), ± are the signs for the torsion angle values.

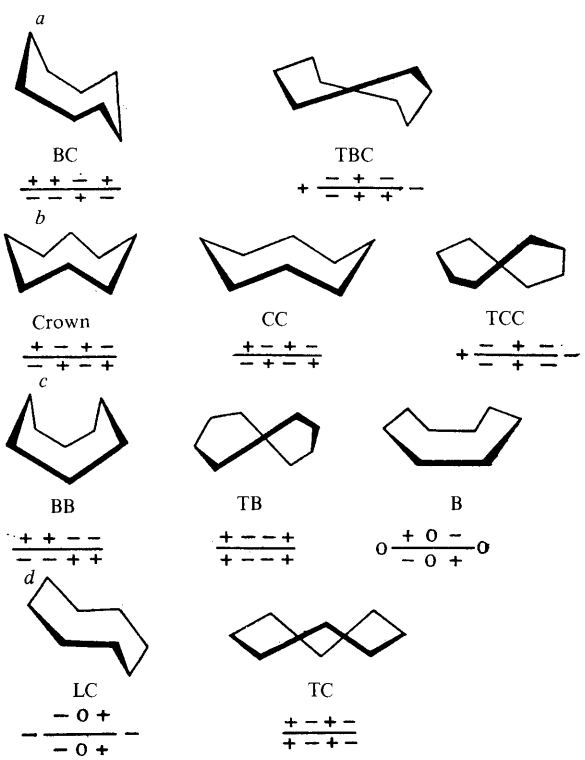


Figure 1. The possible conformations of cyclooctane.[13,14]

In addition to the chemical numbering of the atoms, differentiation of the conformational system has also been proposed for eight-membered rings. This is due to the existence of nonidentical positions in each conformation, which is caused by the unequal distribution of interactions between the chemically nonbonded atoms. For example, when a heteroatom or carbonyl group (which can be labelled X) is introduced, several forms of BC conformation can be distinguished: BC-1, BC-2, ... BC-8. For heterocycles with a single X, conformations BC-2, BC-3, and BC-4 are enantiomeric to conformations BC-8, BC-7, and BC-6 respectively (in the literature isomers with a mirror plane of reflection are indicated by an asterisk—BC and BC*).

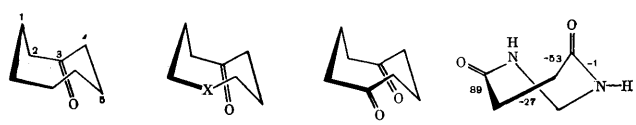


Enantiomeric conformers, like the normal ones, undergo conformational changes as a result of pseudorotation processes (with a partial change in the signs and values of the torsion angles) or inversion (with a partial or complete change in the signs of these angles).[2,14] Sometimes in dynamic NMR spectra it is possible to observe the "freezing-out" of several conformational processes.

The BC form is the preferred conformation of cyclooctane.[2,13,14] Introduction of planar fragments into the *exo* and *endo* positions of the cyclooctane ring affects in different ways the stabilisation of the atoms of the ring in one plane. For *exo* positions (as, for example, in the case of cyclooctanone), as in the saturated rings, three atoms remain in one plane, but in the process the geometrical parameters and torsional configuration about the adjacent bonds change. For *endo* positions, four atoms lie in one plane and one torsion angle is equal to zero. This naturally can assist the stabilisation of conformations with zero torsion angles, as in the B form, especially if two or four planar fragments are introduced into the ring. However, in practice this seemingly indisputable assumption does not always hold. Up to now it remains unclear how the occurrence of planar fragments affects the conformation of eight-membered rings.

2. Mono- and Di-ketones

The simplest example of an eight-membered ring with a single planar fragment is cyclooctanone (I), since the carbonyl group in the molecule can be regarded as a planar fragment that introduces a double bond into the exocyclic position of the molecule. According to the calculations (here and subsequently if a method of calculation is not indicated, conformational energy calculations carried out by means of molecular mechanics are implied) and analysis of the temperature dependences of ^{1}H NMR spectra,[2,16] the most favourable conformation for (I) is BC-3 (or BC-7). The stability of this conformer compared to the other BC forms is due to a reduction in the strong transannular repulsions between the pseudoaxial hydrogen atoms on C(3) and C(7) in the cyclooctane ring. An analogous structure BC-3,7 or BC-7,3 is also established for heterosubstituted analogues with X = 0 (II) and X = S (III).[17,18]

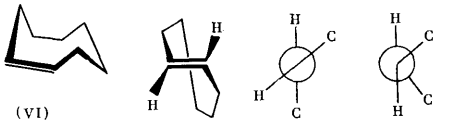


From a study of the temperature dependence of the ^1H and ^{13}C NMR spectra it has been possible to detect in this case two types of conformation process, differing from each by 1.2–1.5 kcal mol^{-1} in energy: a low energy process due to pseudorotation of the form BC-3 ⇋ BC-7 ($\Delta G^{\neq}$ for (I) is equal to 6.3 kcal mol^{-1}, for (II) it is equal to 6.7 kcal mol^{-1}, and for (III) it is equal to 7.8 kcal mol^{-1}), and the high-energy process for the inversion BC-3 ⇌ BC-3* via the chair form with $\Delta G^{\neq}$ barriers for (I)–(III) of 7.7, 8.15, and 9.0 kcal mol^{-1} respectively.[18] Both these processes proceed fairly rapidly in the NMR timescale. When substituents are introduced into the ring, the barrier, as a rule, increases. Thus, in 5-t-butyl-substituted cyclooctanone it is 8.0 kcal mol^{-1}.[19] The slight increase in the inversion barriers in (II) is due to a transannular interaction between the oxygen atom and the carbonyl group. Thus, replacement of one methylene group in cyclooctane by a carbonyl group does not produce any substantial changes in the steric structure of the eight-membered ring.

According to IR[20] and NMR spectroscopic data, cyclooctane-1,5-dione has the same structure in the crystalline state as in solution, corresponding to conformation BC-3,7 (IV).[16] Two dynamic processes with $\Delta G^{\neq}$ barriers equal to 6.1 and 7.0 kcal mol^{-1} were found for its deutero-analogue.[16] The two geometrical isomers of 2,4,6,8-tetrabromocyclooctane-1,5-dione also have the BC-3,7 form, and they differ according to the orientation of the C–Br bonds.[21] Ketones in which a heteroatom is situated at the α-position relative to the C=O group should also formally belong to this group of compounds. However, in the case of 2,6-diazocine-1,5-dione (V) it was shown[22] that they comprise systems with an endocyclic planar fragment formed by C=O groups and NH. Thus, compound (V) should be grouped with compounds that contain two endocyclic planar fragments at the 1,5-position relative to each other (see Section V). The torsion angles found for it correspond to those calculated for the TB form of 1,5-cyclooctadiene (LXI).

3. Cyclooctene Derivatives

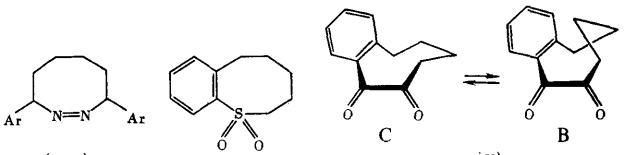
In cyclooctene the ring can be made up in both the *cis*- and *trans*-isomers, and the latter is sufficiently stable to be studied experimentally. It was shown from calculations[23–26] and then also by X-ray diffraction analysis of enantholactam hydrochloride[2] that the most favourable form for the *cis*-isomer is one similar to BC (VI).



(VI) (VII) (a) (b)

In the *trans*-isomer the double bond is highly strained. Calculations predict for it form (VII), namely, twist-chair-chair (TCC) and this has subsequently been confirmed by X-ray diffraction[27,29] and electron diffraction.[30] The double bond is distorted, and the torsion angle is considerably less than 180°: 135.4°,[31] 137.7°,[17] 145.3°,[2,23] 138.0°.[24] This is not a simple twisting of the double bond (*a*) (Newman projection along the double bond), but that in which all six atoms adjacent to this bond are tending to align in one plane (*b*); it has been demonstrated by neutron diffraction that the olefinic hydrogen atoms actually protrude from the plane of the double bond.[2] The torsion angles (φ) along the cyclic bonds in (VII) amount to: 135.4°, –86.5°, 50.7°, and 114.4° (here and subsequently the angle formed by the atoms 8,1,2,3 is given first and that formed by 1,2,3,4 is second, and so on in order).[31] In the case of cyclooctene two conformational processes that occur with barriers of 5.8 and 8.2 kcal mol^{-1} have been found by means of dynamic NMR.[19,32] For the 1-fluoro derivative the barrier is higher according to the ^{19}F NMR spectra and it amounts to 6.1 kcal mol^{-1},[33] while in the *cis*-oxide it increases to 8.0 kcal mol^{-1}.[32]

Among heterocyclic analogues of cyclooctene the *cis*- and *trans*-isomers of 3,8-dialkyl-1,2,-diazocines (VIII) have been discussed,[34] but these results based on a possible equilibrium of *cis*- and *trans*-isomers should be re-examined.[3]



(VIII) (IX) C ⇌ B (X)

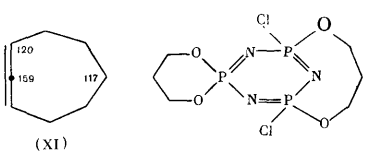
The benzosulphone (IX) has been studied by X-ray diffraction.[35] Introduction of a carbonyl group into the α-position relative to the planar fragment causes them to adopt a coplanar configuration, which has been shown in the case of benzocyclooctene-5,6-dione. In this case five atoms are situated in one plane, and the system becomes analogous to that of cycloocta[d,e]naphthalene (Section III) and its conformational behaviour is such that an equilibrium of C and B forms (X) occurs.

It is evident from the examples given that introduction of a single planar fragment into an eight-membered ring does not lead to substantial changes in its conformational behaviour. For ketones and *cis*-cyclooctenes the most favourable form remains BC as in cyclooctane,[2] and the occurrence of the TCC structure in *trans*-cyclooctene is due solely to steric restrictions that are specific to this case.

III. DERIVATIVES OF 1,2-CYCLOOCTADIENES

1. 1,2-Cyclooctadienes

The calculations made for 1,2-cyclooctadiene (XI)[37] (in the literature there are reports only about attempts to isolate this unstable product in a pure state[38]) revealed two preferred conformers T and TC which have similar energy; their torsion angles and energies are shown in Table 1. The T conformer has a second-order axis of symmetry, and the torsion angles along the cyclic bonds correspond exactly to the T form (see Chapter V). This conformer is defined as TB by the author. The transition barrier between the two forms has been calculated (8.8 kcal mol^{-1}). From the reported values of the bond angles within ring (XI), it is clear that the central allene bond of the molecule is twisted, which produces considerable internal strain in it.



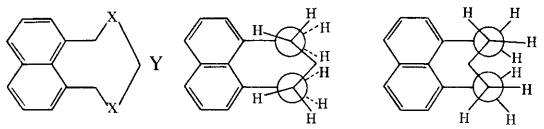
(XI) (XII)

Among heteroanalogues the structure of the inorganic heterocycle (XII) has been studied in the crystalline state.[39] The main structural difference between this molecule and (XI) is determined by the

fact that the central atom in the X–Y–X triad of heteroatoms [see also Chapter VII, compounds (LXXXII) and (LXXXIII)] has a much larger bond angle (about 125°), which is due to the different electronic state of the carbon atom and substituent Y. In the specific case examined, the ring of the *spiro/ansa*-isomer of cyclotriphosphazene (XII) has a BC conformation in which the NP_2O_2 fragment is in the form of a boat.[39] The stability of the BC form is so high that the P(4)N(5)P(6) angle is decreased to 112.7° (this is the smallest of all the values; in a six-membered ring it reaches 124.2°).

2. Derivatives of Cycloocta[d,e]naphthalene

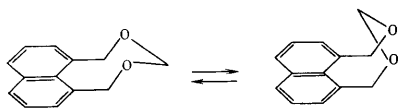
The main feature of compounds of this series [(XIII)–(XVII)] is the occurrence of a *peri* interaction. This dictates the specific type of conformational behaviour that stabilises the B conformation; in it the energy of torsional rotation about the C(1)–C(2) bonds [C(4)–C(5) bonds] is less (skewed conformation) than in the C form.



(XIII)–(XVII) C B

According to the ^{1}H NMR spectroscopic data, the parent carbon compound (XIII) with X = Y = CH_2 and also its deuterated analogue have the B conformation. By studying the temperature dependence it was possible to determine the energy characteristics of the conformational process B ⇌ B*: $\Delta G^{\neq}$ is equal to 14.5 kcal mol^{-1}, $\Delta H^{\neq}$ to 16.1 kcal mol^{-1}, and $\Delta S^{\neq}$ to 5.4 E.u.[40] Introduction of methyl substituents into the X position (X = CMe_2) assists the relative stabilisation of the B form, so that compounds with Y = CH_2 or C=O, even if they have only one *gem*-dimethyl group at the X position, exist exclusively in this conformation. The inversion barriers of the rings increase by 4.8–5.9 kcal mol^{-1} relative to their nonmethylated analogues.[41]

Among the heterocyclic derivatives of this series 1,3-dioxans (XIV) with X = O and Y = CHR have been studied to the greatest extent. For the simplest acetal (R = H), when the energy is minimised with parametrization,[42] two conformations C and B with ΔH_{C-B} of 1.0 kcal mol^{-1} are predicted;[43] according to the ^{1}H NMR data for $CHCl_3$ and $C_2Br_2F_4$ (1 : 1) ΔH is equal to 0.7 kcal mol^{-1}.[44] The existence of a conformational equilibrium follows from the IR spectroscopic data, dipole moments, and ^{13}C NMR spectra of different acetals with R = H, Me, iso-Pr, t-Bu, Ph, *p*-ClC_6H_4, and *p*-$O_2NC_6H_4$.[45]



C (XIV) B

In the 3-t-butyl derivative the value of ΔH increases to 1.4 kcal mol^{-1}; and in the crystalline state, according to the X-ray diffraction data, the C form occurs with an equatorial configuration of the t-butyl group.[46] The C conformation is also typical for sulphate (XV) with X = O and Y = S=O, with the S=O bond exclusively occupying the axial position,[43] as in six-membered sulphates.[5] In acetals the C form is destabilised by the *peri* effect; the increase in nonbonded and torsional strains leads to a relative stabilisation of the B conformation.[46,47]

Replacement of the ring oxygen atoms by sulphur [(XVI) with X = S and Y = CHR] makes this form more favourable in thioacetals, and the proportion of C conformer present is reduced to 7%.[48] In contrast to acetals, ketals (XVI) with X = S, R^1 = R^2 = Me, $(CH_2)_5$ mainly have the C conformation.[48] The subsequent replacement of Y = CR^1R^2 by a sulphur atom gives trithiocines (XVII) with X = S and Y = S, for which dynamic ^{1}H NMR spectroscopy was used to detect an equilibrium of two forms in the ratio 10 : 1 (in pyridine-d_5) which participated in two types of conformational process—a relatively rapid process with $\Delta H^{\neq}$ 15 kcal mol^{-1} and $\Delta S^{\neq}$ −1.1 cal mol^{-1} K^{-1} and a slow process with a higher $\Delta G^{\neq}$ barrier equal to 17.9 kcal mol^{-1}.[49] When calculations were applied to interpret the experimental data it was shown that the B form was more stable than the chair form by 0.6 kcal mol^{-1}. The T conformation is obtained on the energy surface by moving out each $C_{sp^3}-C_{sp^2}$ bond 15° from the plane of the naphthalene ring; this leads to a loss of 13.6 kcal mol^{-1}. The conformational processes detected correspond to the exchange B ⇌ B* via the T form and B ⇌ C.[49]

Thus, the steric structure of an eight-membered ring with two planar fragments in the 1,2-position is determined to a considerable degree by the nature of these fragments. In allene systems twisted forms (T, TC) predominate; replacement of sp^2 carbon atoms by heteroatoms decreases the angle in the ring between the double bonds, which helps to remove strain and the system in terms of its parameters approximates to saturated eight-membered rings (XII). In naphthalene derivatives the *peri* effect together with torsional strain and nonbonded interactions controls the stabilisation of the B and C forms. As was shown above in the case of benzosulphone (IX),[35] these principles are applicable to α-keto derivatives of cyclooctenes.

IV. DERIVATIVES OF 1,3-CYCLOOCTADIENES

Initial calculations of the conformational energies of 1,3-cyclooctadiene (XVIII) identified two preferred conformers, approximately equal in energy and defined as TB.[2,50,51] Subsequent calculations led to more accurate notions of the energetics of these basic conformers and provided a basis for developing their nomenclature.[52] The results of the calculations, the energies, nomenclature, and torsion angles are presented in Table 1. It can be seen from this that two conformers stand out in terms of stability—TBC with C_2 symmetry, which is more stable by 0.5 kcal mol^{-1} than the second form (TB) with C_1 symmetry. The remaining forms are less favourable than TB—the boat by 6.3 kcal mol^{-1}, and the half-chair (HC) and twist form by 8.3 kcal mol^{-1}. The decrease in symmetry of the T form of cyclooctadiene derivatives as compared with the TC conformation depicted in Fig.1 and having C_{2h} symmetry is due to the introduction of planar fragments into the ring. As may be seen from the next chapter, when there is a favourable geometric environment its occurrence is possible [compounds (XLII) and (XLIII)].



TBC TB T B HC

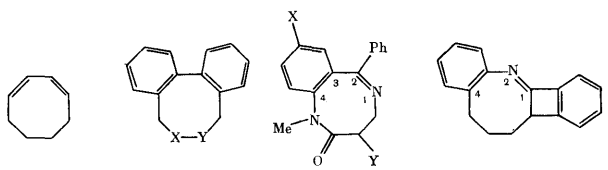
Table 1. The conformations of derivatives of 1,2- and 1,3-cyclooctadienes.

Compound	X	Y	Torsion angles, in deg.*								ΔG^0, kcal mol^{-1}	Notation**	Refs.
			1	2	3	4	5	6	7	8			
(XI)	—	—	—	63	—13	—71	58	—	—	—	14,64	T (TB)	[38]
	—	—	—	68	—75	63	—81	116	—62	—14	14,87	TC	[38]
(XVIII)	—	—	—6	—54	—6	94	—85	59	—85	94	7.12	TBC	[52]
	—	—	—4	—42	—2	92	—52	—59	82	—5	7.66	TB	[52]
	—	—	3	—58	3	28	46	—118	46	28	14.00	B	[52]
	—	—	—	0	—1	65	85	0	—	—	16.30	HC	[52]
	—	—	—	—57	—11	98	—45	—5	—	—	16.25	TBC ⟷ TB	[52]
(XIX)	O	O	3.3	64.9	3.3	—52.1	—31.3	119.5	—31.3	—52.1	—	B	[53, 54]
(XX)	S	S	—	54.32	—	—	—	—	—	—	—	TBC	[55]
(XXI)	O	SO_2	4.3	64.8	—6.7	—90.3	102.6	—64.9	81.3	—92.1	—	TBC (DC)	[54]
(XXII)	S	SO_2	2.1	67.0	2.1	—104.8	86.9	—47.4	86.9	—104.8	—	TBC (DC)	[56]
(XXIII)	Me	Ph	0	—65.9	—12.3	89.2	—31.6	—52.6	7.6	70.2	—	B	[57]
(XXIV)	Br	H	—1.0	—71.6	—3.6	67.3	9.1	—69.3	—12.3	79.4	—	B	[58, 59]
(XXVI)	—	—	—4.2	—56.9	4.9	87.2	—95.7	65.0	—72.2	81.1	—	TBC (C)	[60]

* Torsion angle 1 is formed by atoms 8, 1, 2, 3; angle 2 by atoms 1,2, 3, 4; and so on.

** The labels used by the authors for the conformations are given in brackets; D stands for a deformed conformation, HC is a half-chair, TBC ⟷ TB is a form intermediate between TBC and TB.

From a detailed study of the contributions of different types of strain to the total energy it is possible, in our opinion, to distinguish the angle strain, namely, the strain occurring as a result of bond angle deformation (ΔE_θ relative to the TBC form is 3.3 kcal mol^{-1} for TB, 4.3 kcal mol^{-1} for B, 7 kcal mol^{-1} for HC, and 5.2 kcal mol^{-1} for T). These observations, in the opinion of the author of this review, indicate that the conformational situation can change when heteroatoms, which have bond angle values that are different from those of the carbon atoms and often undergo angular deformations more easily, are introduced into the ring. That is why Table 1 also contains data on torsion angles and conformations obtained by X-ray diffraction analysis for the heterocyclic analogues of 1,3-cyclooctadiene and includes the dibenzo derivatives (XIX)–(XXVI).[53-60] The author's labels for the conformations in Table 1 are given in brackets. For two compounds [(XXV) and (XXVI)] we have calculated the torsion angles from atomic coordinates reported in two articles.[59,60]



(XVIII) (XIX)–(XXII) (XXIII)–(XXV) (XXVI)

It is evident from the data in Table 1 that TBC is the principal form; compounds (XX)–(XXII)[54-56] and (XXVI)[60] exist in it (see also the results for rhazinilam.[61]). The TB conformer was not detected in a single case, but the B form is fairly representative [(XIX), (XXIII)–(XXV) with X = Me, Br, Cl[53,54,57-59]].

On the whole it should be noted that the TBC form has quite high values for the dihedral angles about the bonds formed by the ring atoms 4–5, 5–6, 7–8, and 8–1 (about 80–100°) and with alternating signs. In the TB form the angle values are lower, one of those adjacent to the double bonds is positioned almost in the same plane with it while the other is very twisted [5° and 92° in (XVIII)]. A B conformation very similar to that predicted by calculation for carbocycle (XVIII) is found in peroxide (XIX). In it the bond opposite the single bond and situated between the two planar fragments is very twisted (about 120°). In the other compounds the single bonds adjacent to the double bond (4–5 and 1–8) are more twisted in comparison with the remaining ones. This helps to flatten out the 4–5–6–7 and 6–7–8–1 fragments so that the B form in compounds (XXIV)[58] and (XXVI)[59] approximates to the classical cyclooctatetraene structure[62] (Section VII).

1,3-Cyclooctadiene (XVIII) has been studied in solution by means of ^{1}H and ^{13}C NMR.[52,53] An interpretation of the results obtained for its mono- and di-epoxides has been carried out from data calculated on the energies of the conformers. They exist in a primary state as a mixture TBC ⇋ TB, and the proportion of TB falls on changing to the diepoxide. Three conformational processes with barriers of 7.2 kcal mol^{-1} (7.4 for the monoepoxide), 9.0 kcal mol^{-1} (9.9), and about 10 kcal mol^{-1} were detected by temperature measurements. The first corresponds to the conversion TB ⇋ TB* via the B form, the second corresponds to TB ⇋ TBC. From among the heterocyclic compounds, nonempirical quantum-chemical calculations[4] were carried out for the disulphide (XX) on the basis of molecular mechanics[65] and also the temperature dependencies of the ^{1}H NMR spectra were studied.[66] The TBC form is recognised as the most favourable since quite a high inversion barrier was found ($\Delta G^{\neq}$ 28.8 kcal mol^{-1}, $\Delta H^{\neq}$ 26.6 kcal mol^{-1}, and $\Delta S^{\neq}$ -6.0 cal mol^{-1} K^{-1}).[66] Such high barriers have also been determined for dibenzo derivatives of 6,7-dicarboxy-1,2,3,4-dibenzocyclooctane.[66] It is apparent that, as in seven-membered heterocycles,[2] replacement of a double bond by a benzo fragment produces an increase in the barriers for conformational conversions.

Table 2. Quantitative characteristics of conformers of 1,4-cyclooctadiene and 1,3,2-dioxaphosphocines.

Compound	Conformation	Torsion angles, deg.*								ΔE, kcal mol^{-1}	Folding parameters				
		1	2	3	4	5	6	7	8		q_2	φ_2	q_3	φ_3	q_4
(XXVII)	BC	87	—87	73	0	—85	85	0	—73	12.20	—	—	—	—	—
	BB	—72	72	4	1	—83	83	1	—4	15.91	—	—	—	—	—
	TB-T	54	54	—89	0	26	26	0	—89	1[9] 09	—	—	—	—	—
	DTB**	52	55	—88	4	13	38	—3	—90	12.22	—	—	—	—	—
(XXVIII) Y = UEP	BC	95	—95	80	0	—91	91	0	—80	—	0.46	280	0.86	0	0.23
	BB	—93	93	6	0	—89	89	0	—6	—	1.30	180	0.11	180	—0.38
	B	—110	17	51	0	—96	54	0	59	—	1.38	146	—0.18	282	—0.33
	TB	63	54	—111	0	86	39	0	—64	—	1.33	123	0.36	48	—0.13
(XXVIII) Y=O, S	BC	91	—91	80	0	—90	90	0	—80	—	0.51	0	0.80	180	—0.19
	BB	—88	88	5	0	—88	88	0	—4	—	1.27	180	0.06	180	—0.35
	B	—112	14	55	0	—92	51	0	63	—	1.35	—36	0.18	270	0.30
	TB	66	55	—112	0	83	38	0	—67	—	1.30	123	0.36	46	—0.12

* Torsion angle 1 corresponds to the angle formed by atoms 1,8,7,6 (according to the numbering of 1,4-cyclooctadiene); angle 2 corresponds to atoms 8, 7, 6, 5; angle 3 to atoms 7, 6, 5, 4; and so on.
** D stands for a deformed conformation relative to the ideal form.

V. DERIVATIVES OF 1,4-CYCLOOCTADIENES

1. Basic Conformations

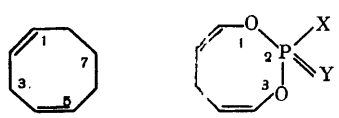
Among eight-membered rings with two planar fragments, derivatives of 1,4-cyclooctadiene (XXVII) have been studied in greatest detail. In this chapter we shall examine the possible conformation of this ring on the basis of the X-ray diffraction data and the quantitative properties of the conformers. 1,4-Cyclooctadiene has been the subject of several theoretical studies,[50,67-70] in which three conformations BC, BB, and TB are considered.



BC BB TB B

Calculations show that BC is the most stable form; its difference in energy from the TB conformation is 0[67] or 1.1 kcal mol^{-1}.[50] The BB form is the transition state in the process TB $\rightleftharpoons$ TB*.[68] Consequently, for (XXVII) the two forms BC and TB are expected to participate. However, as has already been observed above, the situation can alter on changing to heterocyclic analogues.

The basic conformations of compounds of this type have been studied in the case of 1,3,2-dioxaphosphocines with three- and four-coordinated phosphorus[71] (Y is an unshared electron pair (UEP), or an atom of phosphorus or sulphur) using the method of Cremer and Pople[38] developed for eight-membered rings.[9,10]



(XXVII) **(XXVIII)**

Calculations have been carried out using X-ray diffraction data for 4,5;7,8-dibenzo-1,3,2-dioxaphosphocines[72,73] [compounds (XXXV) and (XXXIX) in Table 3]. Four basic conformations were obtained—the three proposed for (XXVII) and a distorted B form. Table 2 gives the torsion angles about the cyclic bonds in compounds of three- and four-coordinated phosphorus (XXVIII) and the folding parameters. In this case the torsion angles of the different conformations of (XXVII) and their relative energies[68] are listed.

Before going on to discuss actual conformers, let us consider Table 3, where the X-ray diffraction data that is available at the present time for the heterocyclic derivatives of (XXVII) have been collected. The compounds (XXIX)–(XLIX) are listed according to the increase in the number of heteroatoms in the ring.[72-87] These are mainly dibenzo derivatives and only two examples relate to compounds with dinaphtho residues [(XXXVIII) and (XXXIX)].[73,80] On correlating the calculated and experimental data we observe that when compounds have the same conformations, regardless of the nature of the heteroatoms, the torsion angles vary over quite a narrow range, so that dihedral angles can be used, in our opinion, as a quantitative criterion of the conformers. As in the case of (XVIII), the BC form has high values of the torsion angles about the single bonds with alternating signs. This form is fairly typical in compounds with a methylene bridge—(XXIX),[74] (XXXV)–(XXXVII)[72,78,79]—or a sulphur atom [(XLIV)], as well as in thiazocinium salts (LI), 1,5-dithiocines (XLIX),[97-99] and dibenzosilocine.[100] In the BB conformation the fragments enclosing the single bonds that are adjacent to the planar groups are very flattened out (torsion angles constitute 3–8°). In this form the substituents occurring at the flagpole position approach very close to each other, which contributes to a destabilisation of this conformation. The relatively small difference in energy calculated for the BB form of (XXVII)[68] is due to a substantial flattening out of the fragment made up by the atoms 8,1,2,3,4 in comparison with the related BC form. At the same time it is possible to change from the BB to a distorted B conformer by a small rotation. Proposals about the possible existence of such a conformation in heterocycles were also put forward previously.[88,89] However, their quantitative parameters

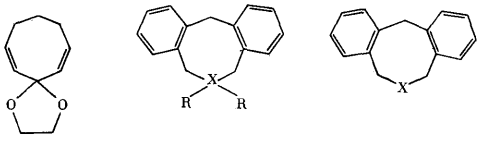
were only obtained recently[71] (Table 2). It was possible to make an unequivocal interpretation of the X-ray diffraction data (Table 3) from a knowledge of the torsion angles. It transpired that this form had been observed by many authors but they had given it arbitrary names. It is typical for azocines (XXX),[75] their sulphur derivatives (XXXI)–(XXXIV),[76,77] 1,3,2-diazaphosphocines (XL),[81–83] and 4,5;7,8-dinaphtho-1,3,2-dioxaphosphocines (XXXVIII) and (XXXIX).[73,80] In some studies this form is also called TB,[76,77] by analogy with a previous study,[88] although it is particularly stressed that this is quite a different conformation from the TB form discussed in the previous studies.[88,89] Thus, only when quantitative criteria were used for the identification of conformers was it possible to avoid ambiguity.

An examination of the T and TB forms deserves particular attention. Even in the basic study of Anet,[68] the dihedral angles for these two forms differed only slightly (Table 2). In the ideal T conformation with the C_2 symmetry, torsion angles 1 and 2 are equal to 60°, and deviations, which are often small (about ±30°) serve to identify the TB form. In the less twisted distorted B conformer these angles have different signs and differ in absolute value by 60–90°. As was predicted in the calculations of Anet[68] and from the folding parameters,[71] this conformation occurs in those cases when the angle at C(6) in the bridge position is readily opened up to 120°. Such a situation must occur in keto derivatives. In fact, the two ketones (XLII) and (XLIII) studied so far[85,86] have a T conformation.

2. Conformational Behaviour in Solution

(a) Derivatives of 1,4-Cyclooctadienes

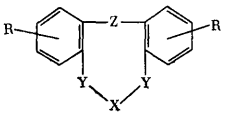
An analysis of the shielding effect from the C(3) atom in the ^{13}C NMR spectra and also the changes in the ^{1}H and ^{13}C NMR spectra on varying the temperature lead to the conclusion[68] that (XXVII) exists as an equilibrium BC ⇋ T (or TB) with an interconversion barrier of 8 kcal mol^{-1}. As a result of the fact that in their studies the authors have not made a distinction between the T and TB forms, the generalised label [TB] is used subsequently in such cases. According to force-field calculations it is proposed that the pseudorotation T ⇋ T* takes place with a very low barrier of 3.8 kcal mol^{-1}.[68]



(XLV) (XLVI) (XLVII)

The ethyleneketal (XLV) is conformationally pure and exists exclusively in the T form, its barrier for pseudorotation is higher than in (XXVII) by 6.0 kcal mol^{-1}.[18] The conformational behaviour of the dibenzo derivative (XLVI) with R = H is considerably different

Table 3. The conformations of dibenzo derivatives of 1,4-cyclooctadienes with the general formula.



Compounds	X	Y	Z	Torsion angles, deg.*								Conformations***	Refs.
				1	2	3	4	5	6	7	8		
(XXIX)	NMe	CH_2	CH_2	−88.6	88.1	−71.5	1.1	86.9	−88.0	0.3	71.3	*a*-BC	[74]
(XXX)	N-tert-Bu	CH_2	CH_2	−115.4	44.1	41.3	−2.8	−91.0	59.4	−3.1	42.3	*e*-B (TB)	[75]
(XXX)	N-tert-Bu	CH_2	CH_2	−64.5	135.9	−41.3	2.8	−59.4	91.0	3.1	−42.3	*e*-B (TB)	[75]
(XXXI)	NMe	CH_2	SCl	140.7	−72.1	−29.1	−3.9	72.7	−69.3	2.8	−22.8	B (TB)	[76, 77]
(XXXII)	NMe	CH_2	SOMe	−142.5	77.3	−25.3	4.8	70.9	68.0	−6.6	26.9	B (TB)	[76, 77]
(XXXIII)	NMe	CH_2	SMe	132.9	−65.7	−34.0	−1.6	83.2	−66.1	6.4	−29.6	B (TB)	[76, 77]
(XXXIV)	NMe	CH_2	S=O	−129.2	69.1	30.8	4.8	−85.9	66.6	−8.8	27.4	B (TB)	[76, 77]
(XXXV)	POPh	O	CH_2	−94.7	95.3	−80.1	−0.1	90.9	−92.5	1.2	−79.2	*e*-BC	[72]
(XXXVI)	$PNPh_2$	O	CH_2	−95.3	97.7	−77.9	−6.0	95.0	−86.8	−1.9	77.9	*e*-BC	[78]
(XXXVII)	$P(S)NEt_2$	O	CH_2	−94.6	93.2	−74.8	−3.5	90.1	−94.3	6.2	75.9	*e*-BC	[79]
(XXXVIII) **	$PNEt_2$	O	CH_2	−110.8	20.9	48.9	−0.4	−96.2	54.2	−1.5	58.2	*e*-B	[80]
(XXXIX) **	$P(S)NEt_2$	O	CH_2	−101.4	1.5	57.5	9.5	−100.7	50.7	−0.9	61.0	*e*-B	[73]
(XL)	P(O, S)Cl	NMe	CH_2	−96.0	6.0	—	—	—	—	—	—	B (DC)	[81–83]
(XLI)	S=O	O	CH_2	−100.1	98.9	−82.2	3.4	85.8	−91.0	2.1	81.5	*a*-BC	[84]
(XLII)	S=O	O	C=O	71.0	57.0	−92.1	−8.0	39.6	17.9	−1.7	96.7	T (DBB)	[85]
(XLIII)	SO_2	O	C=O	67.7	59.7	−94.2	−6.2	42.4	11.1	1.2	−93.7	T (DB)	[86]
(XLIV)	S=O	O	S	−89.8	90.0	−90.7	0.4	86.4	−79.5	−6.9	92.6	*a*-BC	[87]

* Numbering of the torsion angles corresponds to that in Table 2.

** Dinaphtho derivatives.

*** *a* indicates an axial orientation of the exocyclic bond, *e* indicates an equatorial orientation.

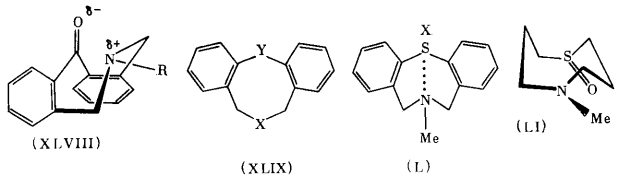
from that of (XXVII);[90,91] the equilibrium BC ⇋ [TB] is displaced 98% towards the first conformer, and the $\Delta G^{\neq}$ inversion barrier between them is much higher (14.9 kcal mol^{-1}), while the barrier for the transition BC ⇋ BC* is even higher (15.3 kcal mol^{-1}).[91] These results are somewhat different from those calculated,[90] according to which the energies of the BC and T forms are equal and the BB form is less favourable than them by 5.3 kcal mol^{-1}. The transition barrier for the process BC → T was also calculated (15.2 kcal mol^{-1}) and its possible pathways indicated.[90]

A change in the nature of the substituents R in (XLVI)—XR_2 = C=O, C=CH_2, CHMe, CHAc, $CMeCH_2OH$, $C(CN)_2$[92]—affects the position of the equilibrium BC ⇋ TB and the inversion barriers to a considerable degree. The population of the TB conformer is essentially small (2–16%). When there is *gem*-substitution it increases to 40–60% [$C(CN)_2$, $CMeCH_2OH$]. As regards the barriers, they increase on changing from a ketone (10.1 kcal mol^{-1}) to a methylene derivative (13–14 kcal mol^{-1}) and then to compounds with XR_2 = CHMe and $C(CN)_2$ (15–16.7 kcal mol^{-1}). The following NMR criteria were proposed for conformational studies on compounds of this class: 1) the flexible T form has a higher entropy than the BC form (ΔS reaches 7 E.u.); 2) the geminal constant ^2J(HH) of the bridge methylene group is determined to a considerable degree by the structure of the ring; for the BC form it is 12–14 Hz, and for the T form it is 19 Hz; 3) in the ^{1}H NMR spectra of the BC form two sets of nonequivalent AB methylene protons occur, and there are two singlets in the exchange T ⇋ T*.[92]

On the whole, it may be stated that replacement of double bonds by aryl residues contributes to an increase in the transition barriers between the BC and T conformers.

(b) 3,4;6,7-Dibenzo-1-azocines and their Heteroanalogues

The first study on dynamic ^{1}H NMR spectra of dibenzoazocines (XLVII) with X = NR_2 and R = H, CN, CH_2Ph appeared back in 1970,[93] but no definite conclusions were then made about the nature of the conformations occurring. This was made possible by a detailed investigation of a series of azocines with R = Me,[94] H, Me, iso-Pr, t-Bu,[95] and CH_2Ph,[88] as well as their carbonyl analogues with a keto group at the bridge position.[96] Dibenzoazocines are conformationally heterogeneous and are characterised by the equilibrium BC ⇋ [TB]. The latter conformation, enclosed in brackets, denotes that its structure has not been established conclusively, and in some studies preference is given to a T conformer with C_2 symmetry[94–96] while in others an asymmetric TB form is preferred. In some cases a BB conformation is considered.[101] The energy factors of the methyl-substituted amine (R = Me) have been obtained (ΔH –3.2 kcal mol^{-1}, ΔS –7 E.u., inversion barrier 15.3 kcal mol^{-1}).[94] The proportion of [TB] conformer increases as the size of the substituent on the N atom increases (in $CDCl_3$—however, the opposite effect was found in CF_3COOH); when R = H the BC conformation occurs with barrier for the transition *e*-BC ⇋ *a*-BC of 16.1 kcal mol^{-1}, when R = t-Bu the barrier is 16.5 kcal mol^{-1},[95] when R = CH_2Ph it is 17.0[88] or 17.4 kcal mol^{-1};[96] on protonation the barriers increase.[95] For aminoketones with R = CH_2Ph and Me, proper consideration was given for the first time in the literature to the distorted B form (XLVIII),[88,96] which is stabilised in these particular examples by a specific transannular interaction between the N atom and the carbonyl group.

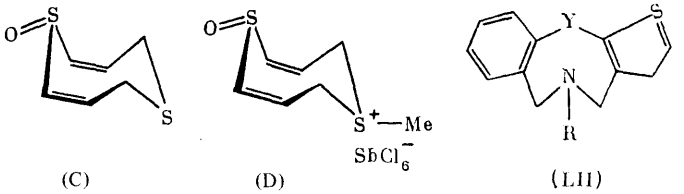


The signals from the two methylene groups in this minor form appear as a singlet at –100 °C, so the authors conclude that the compounds have the B form that occurs during the pseudorotation B ⇋ B* with a barrier of ~8 kcal mol^{-1}. Theoretical calculations carried out for *N*-methylazocine[88,96] show that the BC conformation is actually preferred (ΔE ~4.30 kcal mol^{-1}), and then in increasing energy B (5.54 kcal mol^{-1}), T (5.62 kcal mol^{-1}), and BB (5.94 kcal mol^{-1}). Thus, there is still an open question concerning the steric structure of the minor conformer since the energies of the B and T forms are similar. In our opinion, the use of new, recently obtained spectral criteria of the distorted B form will help to resolve this problem also for azocines (see below).

A fairly extensive group of compounds studied is made up by the heteroanalogues of azocines, in particular thiocines (XLVII) with X = S and SO_2. In the ^{1}H NMR temperature spectra of the sulphone X = SO_2, the protons at C(5) and C(7) appear as an AB system, which is an indication that the BC conformation predominates in the equilibrium BC ⇋ [TB][88] with an inversion barrier of 16.2 kcal mol^{-1} [96] and 15.8 kcal mol^{-1}.[88] According to calculations, the BC form is more favourable in the sulphide than in azocine itself. Introduction of heteroatoms into the bridge position (Y = O, S, SO_2) for those compounds with X = S, SO_2 NCH_2Ph already considered has little effect on the conformational behaviour of (XLIX) compounds, which is manifested in the same dependence on temperature for the NMR spectra.[88] It is therefore concluded that they also exist in the equilibrium BC ⇋ [TB]. The values of the barriers in (XLIX) in relation to the nature of X and Y are given in Fig.2.[88] It can be seen very clearly from it that the energy barriers are determined to a greater extent by the nature of the bridging group Y. The lowest values occur for O-derivatives (10.5–14 kcal mol^{-1}), they are somewhat higher for the CH_2 group (14–16 kcal mol^{-1}), and even higher for the SO_2 group (16–18 kcal mol^{-1}), while for sulphides there is a wide range of barrier values from 12.5 to 16.5 kcal mol^{-1}. As regards the effect of the X group, it is shown less clearly, and it can only be stated that in all of the examples studied the barriers for the sulphones are lower than for the sulphides.

The problem concerning the conformation of the minor component can be resolved in the case of dibenzo-1,5-thiazocines by analysing the current literature; because of the lack of conformity in the terminology this is initially difficult to understand. The authors who hold the opinion that the T form occurs define it as TB;[92,94,95] the same label is given in those cases where a distorted B conformation is being considered.[76,77] Let us consider the data in Table 3 once again. Only for one of the azocines listed there [(XXIX)] is the BC conformation observed in the crystalline state,[74] in all of the remaining cases [(XXXI)–(XXXIV)] the B form occurs,[75–77] while in the thiazocinium salts (XXXI)–(XXXIII) of type (L) this conformation can be recognised as constrained by the transannular $R_3N...SX$ interaction, where sulphur has a trigonal bipyramidal structure. In saturated systems this type of interaction also occurs in the BC form of (LI).[97] However, on going to the dibenzo analogues, such a form where opposing N and S atoms are situated on the base

of the boat cannot occur because of the presence of planar fragments. In the two remaining cases—azocine (XXX) and its sulphoxide (XXXIV)[75-77]—stabilisation of the B form is caused for no other reasons than the inherent properties of this system. In solution (benzene-d_6), according to variable temperature ^{1}H NMR spectra, the sulphoxide retains its structure (the protons of the methylene groups appear as an AB system with ^2J(HH) of 15 Hz at 3.18 and 3.42 ppm).[98] In the thiazocinium salts (L) the S...N attraction is high enough for the B form to be retained even in solution,[77,98,99] and it is predominant although in some cases the presence of the BC conformer is detected (up to 45% depending on the experimental conditions[97]). In the opinion of the authors, when the distorted B form occurs the protons of the methylene group appear as a singlet in the region 3.88–4.25 p.p.m. In 1,5-dithiocines the situation is different; there is an AB system in the spectrum with quite a high $\Delta\delta$ value (0.5–0.8 p.p.m.) and geminal constant of 14–15 Hz, which is associated with the BC conformation of compounds (C) and (D):[99]



(C) (D) (LII)

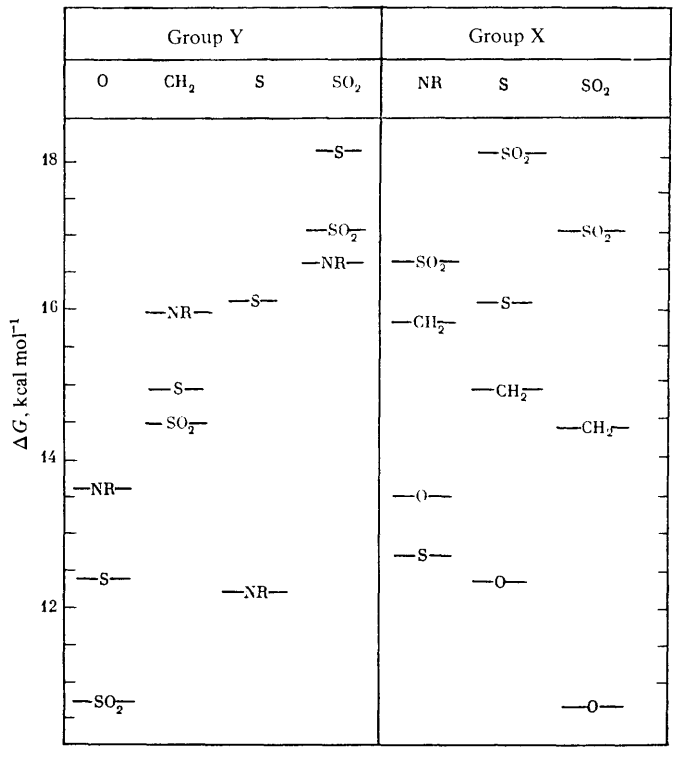


Figure 2. The correlation between the activation barriers $\Delta G^{\neq}$ for the process BC ⇋ B and the nature of groups X and Y;[88] R = CH_2Ph.

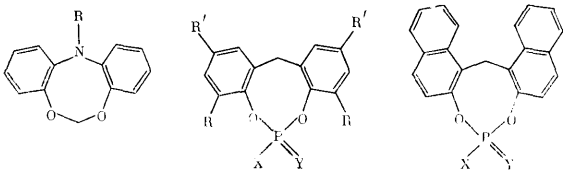
The differences in the conformational behaviour of 1,5-thiazocine and 1,5-dithiocine S-oxides have formed the basis for an explanation of the differences in their reactivity towards electrophiles due to the transannular participation of the amino fragment.[99,102]

There are reports in the literature about the synthesis of benzothienoazocines (LII),[103] 1,5-aza-,[104] and 1,5-oxa(thia)-phosphocines (XLIX) with X = NR, O, S and Y = P(O)R;[105,106] and proposals about their steric structure—whether the BB or TB conformations occur—were deduced by constructing Stewart–Brigleb models. These compounds are very interesting from the point of view of studying the hypervalent bonding of the 1,5-heteroatoms and they will therefore be the subject of future investigations.

On the whole, by examining the conformational behaviour of 3,4;6,7-dibenzoazocines and their 5-heteroanalogues the following conclusion can be made. Despite the discussion which had developed in the literature about the reason for the steric structure of the minor conformer (in certain examples the predominant one), sufficient practical data have so far been accumulated to give preference to a B form that is distorted in one or other direction depending on the geometric parameters of the cyclic fragment. A subsidiary 1,5-transannular interaction helps to stabilise this very conformation. The main competitor to the B form is the BC form, stabilisation of which occurs in compounds that are free of the subsidiary steric interactions.

(c) 4,5;7,8-Dibenzo-1,3,2-dioxaphosphocines and their Heteroanalogues

Compounds of this series have been studied in sufficient detail, which is due to their synthetic asscessibility[101,107] and valuable practical properties.[107-109] Comparatively recently 4,5;7,8-dibenzo-1,3,6-dioxazocines (LIII) were synthesised and their stereochemistry has been studied by means of IR, ^{1}H and ^{13}C NMR, dipole moments, and quantum-chemical calculations using the PPDP/2 method. The latter have also provided the main criterion in selecting the preferred conformer—the BC form. As regards the BB conformation, it has been accepted as not likely to exist[108] because of the strong steric interactions between the methylene and NR groups. It is quite difficult to make definite conformational correlations from the ^{1}H NMR spectra in the compounds examined; a much wider range of possibilities can be admitted in this form of compound with a bridging methylene group, in particular 1,3,2-dioxaphosphocines with different planar fragments (LIV) and (LV).



(LIII) (LIV) (LV)

The spectroscopic characteristics of the CH_2 group [the difference in chemical shift of the protons, geminal ^2J(HH) and long-range ^5J(PH) constants] are closely related to the conformational parameters. Even before the commencement of structural studies, methods had been developed for obtaining compounds of series (LIV) with three-coordinated phosphorus and X = OR,[109] Cl,[110] NR_2[111] and four-coordinated phosphorus with X = H, Y = O,[109,112] X = Cl, Y = S,[113] X = H, Y = S,[114] X = OH, Y = O.[115] The possible steric forms of the cyclic fragment have been examined by means of the folding parameters (Table 2). When these were correlated with the

X-ray diffraction data (Table 3) it was possible to determine the most probable forms—the BC and B conformations. In considering the steric structure of 1,3,2-dioxaphosphocines, one of the main points is also the question concerning the orientation of the exocyclic substituents on the phosphorus atom (we shall take substituent X as a starting point in labelling the conformations). Doubling the number of conformers definitely complicates the solution to the conformational problem, but in many cases, when one form is stable, more reliable conclusions about the steric structure can be made.

Table 4. ^{1}H NMR spectroscopic parameters (δ, p.p.m.; *J*, Hz) of 1,3,2-dioxaphosphocines.[119–121]*

Compound	X	Y	R	$\delta(H^A)$	$\delta(H^B)$	Δδ	^2J(HH)	^5J(PH)
(LIV)	Cl	UEP	tert-Bu	3.68	3.97	0.29	12.6	2.4
	NEt_2	UEP	tert-Bu	3.25	4.31	1.06	12.1	2.3
	NPh_2	UEP	tert-Bu	3.30	4.27	0.97	12.7	5.1
	OEt	UEP	tert-Bu	3.24	4.22	0.98	12.3	3.2
	OPh	UEP	tert-Bu	3.41	4.18	0.77	12.6	2.3
	OC_6H_4-*o*-tert-Bu	UEP	tert-Bu	3.40	4.28	0.88	12.8	2.3
	O-naphthyl	UEP	tert-Bu	3.51	4.39	0.88	12.8	2.7
	OPh	UEP	$C_6H_4CH_3$	3.38	4.29	0.91	12.8	3.0
	NEt_2	S	tert-Bu	3.31	4.12	0.81	12.6	3.4
	OEt	S	tert-Bu	3.65	4.52	0.87	14.6	—
	H	O	tert-Bu	3.61	4.39	0.78	14.0	—
	H	O	$C_6H_4CH_3$	3.66	4.42	0.76	15.0	—
(LV)	NMe_2	UEP	—	5.12	4.56	0.56	15.9	3.5
	NEt_2	UEP	—	5.06	4.54	0.52	16.3	3.6
	OPh	UEP	—	5.06	4.45	0.61	16.0	—
	NEt_2	O	—	5.28	5.03	0.25	15.6	—
	NEt_2	S	—	5.22	5.12	0.10	16.2	—

*The chemical shift from Me in the benzene ring varies within the limits 2.24–2.30 p.p.m.; that from t-butyl varies within 1.22 to 1.38 p.p.m.

Some ideas about the preferred conformations were provided by nonempirical quantum-chemical calculations of the conformational energies in derivatives of a series of (XXVIII) in which the dibenzo fragments are replaced by double bonds. Calculations were made for 2-chloro-, 2-methoxy-,[116] and 2-hydro-2-oxo-1,3,2-dioxaphosphocines.[117] They showed that the most favourable form is the *e*-BC conformation. The most unstable is the BB form with *e*-X and to an even greater degree with *a*-X because of the close contact between the C(6), *a*-H on C(6), and P(2) atoms. Destabilisation increases if the substituent on P(2) occupies the *a* position. As regards all the other conformations, the differences in energy between them were not large enough for definite conclusions to be made, especially as the calculations were made for model compounds without optimisation of geometry and calculation of the effect of the medium.

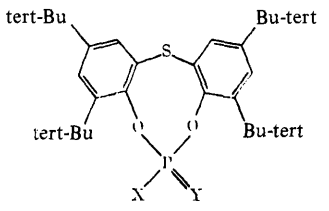
In actual systems studied, the planar fragments are as a rule aryl or naphthyl rings, so it is difficult to expect an absolute convergence of the experimental data and that obtained from calculation.

When we come to consider the spectroscopic characteristics of 1,3,2-dioxaphosphocines, we can turn our attention to the long-range ^5J(PH) constant in azocines. It was originally detected in trivalent phosphorus compounds,[101,118] on the basis of which it was concluded that the BB conformation occurred since the P and H atoms in it are spatially converged. However, as was indicated above,[108,116] the possible occurrence of this structure is very problematic. A single occurrence of this constant cannot yet provide the basis for such a conclusion. Identification of the conformers of 1,3,2-dioxaphosphocines (LIV) and (LV) was made possible from variable temperature ^{1}H NMR spectra.[117,119,122] The spectra of individual conformers were obtained for two of them.[117,122] This assisted the search for spectral criteria of the different conformations. In the ^{1}H NMR spectra the resonance signals from the methylene protons occur in the region 3.24–4.39 p.p.m. for the (LIV) series and at 4.45 to 5.28 p.p.m. for the (LV) series[119–121] (Table 4). They form an AB system, and the low-field doublet in many compounds of the (LIV) series and the high-field doublet in the series of (LV) compounds are split due to long-range interaction with the ^{31}P nucleus. In almost all of the dibenzo derivatives (LIV), with the exception of the phosphorochloridite, a significant (about 1 p.p.m.) nonequivalence (the difference in chemical shifts Δδ) was found in the protons of the methylene group. In addition to the phosphorochloridite, a small Δδ value is also typical for the dinaphtho derivatives (LV). The compounds also differ to a considerable degree with respect to their ^2J(PH) values—12–13 Hz for most of the (LIV) series and 14 to 16 Hz for (LV). Among the P(IV) derivatives of (LIV), ^5J(PH) coupling occurred in one case with X = NEt_2 and Y = S.[122] The spectra of individual conformers were obtained for the phosphorochloridite of (LIV) with R = t-butyl, R′ = Me[117] and the phosphorothioate with X = OEt and Y = S respectively.[122] The energy parameters of the conformational processes of these two compounds were determined: ΔG^0_{195} 0.1 kcal mol^{-1}; $\Delta G^{\neq}_{235}$ 10.85 ± 0.7 kcal mol^{-1} for the first and 0.74 and 12.2 kcal mol^{-1} for the second. In 2-hydro-2-oxo-1,3,2-dioxaphosphocines of (LIV) with R = t-butyl, cyclohexyl, R′ = Me when the temperature was reduced from −40 to −60 °C, there was a sharp increase in Δδ, which corresponds to a slowing down in the intramolecular exchange process with $\Delta G^{\neq}_{220}$ 10.4 ± 0.7 kcal mol^{-1} between the forms,[117] one of which is present in only a small proportion (~10%). In contrast to the dibenzo derivatives, in the (LV) series as the temperature was lowered a regular increase in the difference Δδ was detected, although the spin-spin coupling constant remained virtually constant. This indicates that forms having the same conformation of the cyclic fragment and differing in the orientation of the substituents on the phosphorus atom are taking part in an equilibrium.[120,121] In order to identify the conformers, a quantitative determination of the effect of magnetic anisotropy and electric field of the substituents on the magnitude of Δδ was carried out,[123–125] and also on the contribution from the hyperconjugation effect ΔJ^{π} to the constants ^2J(HH) and ^5J(PH) in the different conformations.[119–121] It was this treatment of the stereospecific nature of the constants in conjunction with dipole moments data that made it possible for the first time to establish spectroscopic criteria for the individual conformers: *e*-BC is characterised by ^2J(HH) of ~12.5 Hz, $^5J(P^{III}H^B)$ and $^5J(P^{IV}H^B)$ are of the order of 3.5–4.0 Hz, Δδ is 1 p.p.m. In the alternative *a*-BC conformation, ^5J(PH) is ~0–2 Hz and the signs for Δδ (H^AH^B) are reversed. Therefore, when there is an equilibrium *e*-BC ⇋ *a*-BC, Δδ is not large (0.2–0.5 p.p.m.), and ^5J(PH) has lower values (1–2 Hz). The *e*-B form has ^2J(HH) of ~14–16 Hz and $^5J(P^{III}H^B)$ of the same order as in the *e*-BC form, but it is less well displayed in P(IV) compounds, Δδ sometimes reaches 1.3 p.p.m.; in the *a*-B conformation ^5J(PH) also cannot be seen. In the equilibrium *e*-B ⇋ *a*-B, as equally in *e*-B ⇋ *e*-BC, Δδ is averaged out and has low values (as a result of the exchange between the *a*, *e*, and *e*′, *a*′ protons). It can be assumed that in the case of compound (LIV) with X = NEt_2, Y = S, R = t-Bu direct evidence has been obtained for the first time for spectroscopic properties of the *e*-BC

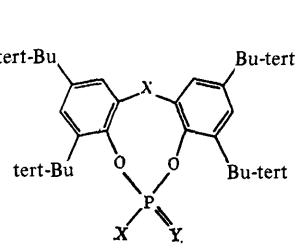
conformer. The compound is conformationally pure in solution, and according to the Raman spectra its steric structure is retained when going from the crystalline form into solution,[126] and its structure in the crystalline state (*e*-BC conformation) has been demonstrated by X-ray diffraction analysis.[79] Similar results have also been obtained for the phenyl phosphite of (LIV) with X = OPh, R = t-Bu, the main conformation of which in solution[119] corresponds to that found in the crystalline state (*e*-BC).[72] An equilibrium of the type *e*-BC ⇋ *a*-BC with a small content of *a*-conformer is also typical for the other dibenzo derivative phosphites with X = NPh_2, NEt_2, OEt, and O-naphthyl. In the phosphorochloridite the population of the second form reaches approximately an equal level (56:44%). In the dinaphtho derivatives of (LV) the BC and BB forms are unlikely to occur because of strong steric repulsions of the α-hydrogen atoms of the neighbouring naphthyl fragments. In the crystalline phase the 2-diethylaminophosphite (XXXVIII) and the diethylaminophosphorothioate (XXXIX) have the *e*-B form.[73,80] The small value of Δδ, ^2J(HH) of ~15.5 Hz, and ^5J(PH) of ~0 Hz must correspond to an equilibrium of the type *e*-B ⇋ *a*-B in the case of P(V) compounds, and similar results have been obtained experimentally. In P(III) compounds the population of the *e*-B conformer is greater with X = NR_2 and less with X = OPh than the *a*-B form.[120,121] If the results obtained for compounds (LIV) with X = H, Y = O[117] are considered in these terms as well as taking into account dipole moment data, a three component equilibrium *e*-B ⇋ *e*-BC ⇋ *a*-BC with population ratio 47:43:10 is acceptable. If the B form is consistent with a geminal constant of 15.6 Hz and the BC form with 12.5 Hz, with the population level of conformers occurring the constant must appear as 14 Hz in the spectra, which is in accord with experiment. The sudden changes in Δδ observed in the variable temperature spectra are due to freezing out of the *a*-BC conformer, which has a Δδ value that is opposite in sign relative to the *e*-B and *e*-BC conformers. The phosphorothioate of (LIV) with X = OEt, Y = S, R = t-butyl exists as an equilibrium mixture of two conformers with population ratio 86:14. In this case the spectral parameters of the minor conformer is consistent with the *a*-BC form (as in the conformationally pure diethylaminophosphorothioate): ^2J(HH) 12.2 Hz, ^5J(PH) 3.5 Hz, Δδ 0.78 p.p.m.; and the predominant conformer is the *a*-B form; 15.5 Hz, 0 Hz, and 1.33 p.p.m. respectively.[122]

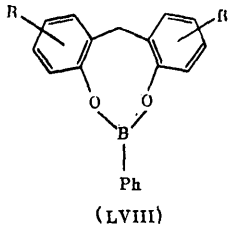
An examination of the spin-spin coupling constants ^nJ(PC) was carried out for the 1,3,2-dioxaphosphocines (LIV) and (LV) considered here in order to establish ^{13}C NMR spectroscopic criteria of use in conformational studies.[121,127] The application of observations reported in the literature concerning the stereospecific nature of the $^2J(P^{III}OC_{sp^2})$ constant[128-130] to the four cyclic conformations led to the conclusion that in the BC form the constant (6.6−6.8 Hz) is greater than in the B conformation (1.5−2.2 Hz).[121,127] The vicinal constants $^3J(POC_{sp^2}C_{sp^2})$ are not large; zero values for (LV) and 2.9−4.4 Hz for (LIV) were obtained with P(III) and somewhat higher values with P(IV). They were correlated with the stereospecific dependences of the $^3J(POCC_{sp^3})$ constants.[131-133] In 1,3,2-dioxaphosphocines the dihedral angle in the POCC fragment is close to 0° in the BB conformation (6°). It is for this type of *cis* orientation that the maximum values for the constant can be expected (of the order of 10−15 Hz). In the *a*-BC conformation a constant close to zero should occur since the dihedral angle has a value of about 90° (80°). In the remaining conformations the order of magnitude of the spin-spin coupling constants is: ^3J(B) > ^3J(TB) > ^3J(*e*-BC). Since from a comparison of the correlations made with the experimentally found values the BB form can be excluded from consideration, it may be assumed that for the first time direct experimental evidence for the absence of the BB conformation has been obtained using ^{13}C NMR spectroscopy.[127] The dihedral angles in the $POCC_{(4)}$ and $POCC_{(2)}$ fragments are related by the equation $\theta(PC_{(4)}) = 180° - \theta(PC_{(2)})$; both angles θ are equal (~90°) in the case of the BC conformation, so the equal value of the two vicinal constants (3.7−4.4 Hz) can serve as a spectroscopic criterion for the BC form. The equality was also found experimentally in dibenzo-1,3,2-dioxaphosphocines (LIV) with P(III).[121,127] As regards the long-range spin-spin coupling constants ^4J(PC) and ^5J(PC), it is difficult at present to make definitive conclusions since the stereochemical relationships have not yet been determined for these constants. In the systems investigated the constant $^4J(PC_{(1)})$ is observed in those cases where ^5J(PH) also has a zero value. However, the reverse does not always occur; the $^5J(PC_{(6)})$ spin-spin coupling constant is as high as 1.5−2.2 Hz in compounds that have a BC conformation.

^{1}H and ^{13}C NMR spectroscopy have been extensively used to study the conformational behaviour of 1,3,2-dioxaphosphocines of the (LIV) series, containing benzene rings into which two t-butyl groups, R = R′ = t-Bu, have been introduced (into the *meta* position relative to the bridging group), and the bridge is an alkylmethylene group CHR (X = OR,[101,134,135] Cl,[119,136] Ph.[136] Bicyclic systems with a POXOP bridge have been reported,[101] and also the corresponding pentaoxyphosphoranes,[134,137] sulphides (LVI) [137-139] with P(III) and X = Cl, Ph, OMe,[139] with P(IV),[139] and with P(V).[137]



(LVI)



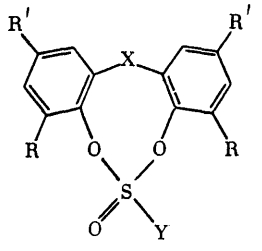


(LVIII)

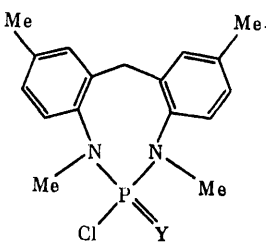
The ^{1}H NMR spectra of the P(III) phosphorus compounds are similar to those reported above for the (LIV) series, and from the existence of a long-range ^5J(PH) constant, the possible occurrence of the BB conformation was proposed.[101,136] In pentaoxyphosphoranes pseudorotation was detected with $\Delta G^{\neq}$ equal to 15.4−15.7 kcal mol^{-1} depending on the nature of the alkoxyl groups at P(V).[135-137] The eight membered ring occupies a diequatorial position in the trigonal bipyramid of the P(V) atom, and pentaoxyphosphoranes with a sulphide bridge have a BC structure.[137] When the temperature is lowered, the doublet of the methylene group (with chemical shift 3.75 p.p.m. and a ^5J(PH) coupling constant equal to 2.7 Hz) from one of the phosphoranes with X = CH_2CF_3 splits into two doublets with chemical shifts 3.52 and 4.11 p.p.m. and ^5J(PH) 1.9 and 2.8 Hz,[135] indicating the presence of a conformational equilibrium.

Recently studies on dibenzo-1,3,2-dioxasilocines (LVII)[139-141] and dibenzo-1,3,2-dioxaborocines[119] were begun. In the methyl derivative of (LVII) with an $SiMe_2$ fragment, the methyl groups are equivalent at room temperature but below 6 °C they become nonequivalent; $\Delta G^{\neq}$ for the process is 13.9 kcal mol^{-1}. The ^{13}C NMR spectra of this compound also change with temperature, and as regards the protons of the methylene group, above T_{coal} they appear as a singlet with δ = 4.12 p.p.m. while below it they appear as a doublet with δ = 3.61 and 4.50 p.p.m., $\Delta\delta$ = 0.89 p.p.m., ^2J(HH) = 14 Hz.[139] The authors came to no definite conclusions about the conformational behaviour (in their opinion there could be BC or BB forms having a plane of symmetry or an equilibrium between identical asymmetric conformations). The inversion barrier in 1,3,2-dioxaborocine (LVIII) is of the same order of magnitude (14.4 kcal mol^{-1}). Since the methylene group in this compound at room temperature appears as a doublet at 3.81 and 4.27 p.p.m. with a geminal constant of 13 Hz, it is suggested that the conformations of (LVII) and (LVIII) are similar.[118] It will be possible to reach definite conclusions about the steric structure of the compounds when detailed variable temperature measurements are carried out, taking into account the spectroscopic criteria (indicating the definite presence of the BC conformer) found in the case of 1,3,2-dioxaphosphocines.

There are also similar spectroscopic parameters for sulphites (LIX) with X = CH_2 and Y = UEP (δ 3.52 and 4.27 p.p.m., ^2J(HH) 12.6 Hz for one of them) existing as equilibrium mixtures given by *a*-BC $\rightleftharpoons$ *e*-BC, and the *e*-BC form predominates when R = Cl, R′ = H and R = t-Bu, R′ = Me, the *a*-BC form predominates when R = R′ = H.[142] In accordance with the spectroscopic criteria found,[120] the dinaphthosulphite with δ 4.64 and 4.84 p.p.m. and ^2J(HH) 16 Hz was assigned the *e*-B form.[142] When the methylene group is replaced by a carbonyl (X = C=O) an equilibrium between the *a*-BC and [TB] forms occurs,[143] whereas the corresponding sulphate with Y = O is conformationally pure and has the BC conformation.[143] These conclusions were based on the IR and ^{13}C NMR spectra. The authors claim that the presence of seven lines in the latter is an indication that the molecule has a plane of symmetry.



(LIX)



(LX)

However, since, as was indicated above, such a situation is also possible with a rapid pseudorotation of the type T $\rightleftharpoons$ T* or B $\rightleftharpoons$ B*, it should once again be considered whether the same conformation that was found for the molecule of this sulphate in the crystalline state is retained in solution.[86]

As in the case of 1,3-dioxaphosphocines a reasonable amount of attention has also been given in the literature to diazaphosphocines (LX).[81,144] The phosphorochloridate with Y = O is conformationally heterogeneous; in the ^1H NMR spectra at low temperatures its methyl groups on the two N atoms are nonequivalent. This may be because the compound either retains the distorted boat conformation found in the crystalline state[71,81-83] or in solution a simultaneous inversion of the two nonplanar nitrogen atoms is occurring in it.

In concluding this Section it may be observed that the results obtained made it possible to establish clearly the effect, caused by the nature of the planar fragments, of exocyclic substituents and the electron configuration of three heteroatoms on the conformational behaviour of derivatives of 1,4-cyclooctadienes. The criteria developed in this case can be used to undertake the conformational analysis of other systems of a similar type. In dibenzo derivatives the most favourable conformation in the majority of cases in the BC form, although in some situations a distorted B form also occurs. Less varied in the conformational sense are dinaphtho derivatives; introduction of two bulky planar groups into them destabilises the BC conformation and the distorted B form becomes more typical. Therefore dinaphtho derivatives can be used as specific models for investigation of B conformers of this type.

VI. DERIVATIVES OF 1,5-CYCLOOCTADIENES

The stereochemistry of 1,5-cyclooctadiene (LXI) has been examined repeatedly in calculations with several force-fields.[67,70,145-148] The energy minimum here corresponds to the TB conformer with C_2 symmetry. The C conformation with C_{2h} symmetry is less favourable than it by 4.09 kcal mol^{-1} [148] or 1.45 kcal mol^{-1}.[145] The differences in ΔE are due in this case to the different values of the dihedral angle ω_3 (Table 5) obtained by calculations with different force fields and energy minimisation procedures. It is claimed that in such cases the Newton–Raphson method is more accurate in determining the minimum.[2,148] The angle ω_3 calculated for the TB form is 52.5°[148] or 37.9°,[145] and the first value is close to that found by electron diffraction for (LXI) with R = R′ = H[149] and by X-ray diffraction for its *syn*-3,7-dibromo derivative with R = H, R′ = Br (LXI)[157] and 4,8-dimethyl-3,7-dicarboxamide derivative with R = Me, R′ = $OCNH_2$ (LXI).[158]

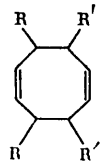


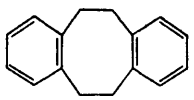
TB B C T

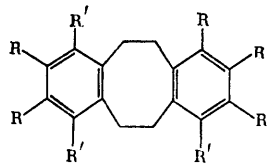
A similar structure was also determined for several organometallic complexes of (LXI),[152,153] dibenzodiazocines,[154-156] and dibenzosilocine.[157] In this conformation there is quite a substantial interaction between the chemically nonbonded H atoms on C(3) and C(7) (distance H...H is 1.992 Å). The energy of the C form is higher because of unfavourable torsional strain along the two types of single C–C bond in comparison with the TB conformer.

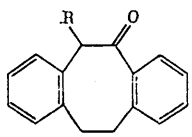
When the double bonds are replaced by benzene residues to give (LXII) (so-called 6,8,6-systems), according to the calculations the difference in energy between the TB and C forms decreases to 1.30 kcal mol^{-1} [145] and the boat form is less favourable by only 0.59 kcal mol^{-1}. This difference in conformational behaviour between compounds with double bonds and those with aromatic fragments is due to the difference in torsional interactions along the $C_{sp^2}-C_{sp^3}$ bonds. In diene systems H/H shielding occurs, with an energy estimated at 1.98 kcal mol^{-1}. Since in the dibenzo derivatives the H/C_{sp^2} shielding is less than 0.5 kcal mol^{-1} in energy,[145] in the latter a pseudorotation process readily occurs while in the

dienes inversion occurs. Introduction of methyl groups into the *o*-position of the benzene rings considerably destabilises the TB form, making the C and B conformers more favourable, and moreover, the transition barriers increase substantially.[154]


(LXI)


(LXII)


(LXIII)


(LXIV)

On turning to an examination of the conformational behaviour of these types of compounds in solution, we should note that when variable temperature ^1H and ^{13}C NMR spectra of (LXI) were recorded two processes with low barriers of 4.4 and 4.9 kcal mol^{-1} were detected.[146] On the basis of calculations of potential energy profiles Ermer asserts that the low-energy barrier corresponds here to the exchange TB ⇋ T ⇋ TB (calculated as 4.15 kcal mol^{-1} at 100 K), while two other processes occur, according to the calculations, via an intermediate boat or chair state with similar barriers of 5.73 and 5.91 kcal mol^{-1}. The experimentally determined barrier of 4.9 kcal mol^{-1} [146,148] apparently corresponds to a combination of these processes. *syn*-3,7-Dibromo-1,5-cyclooctadiene (LXI) with R = H, R′ = Br retains the TB form both in solution and the crystalline state.[150]

The first studies of dynamic ^1H NMR spectra of dibenzo derivatives showed that compound (LXII) was conformationally heterogeneous[159] and two processes for it were found with energies of 7.5 and 10.2 kcal mol^{-1}. At a normal temperature a mixture of TB and C conformations is observed in this case with a predominance of the former.[159] The effect of *o*- and *m*-methyl groups[158,160,161] and of tetra- and hexa-methyl substitution[159] on these processes was also studied. For all of them the equilibrium TB ⇋ C was characteristic, and in the *o,o,o′,o′*-tetramethyl derivative (LXIII) with R = H, R′ = Me the population ratio was 88 : 12 and the interconversion barrier proved to be higher (12.1 kcal mol^{-1}) than in the unsubstituted compound. Thus, the presence of *o*-substituents in this case leads to an increase in energy of the transition state. If four methyl groups are introduced into the *m*-position [(LXIII) with R = Me, R′ = H, the inversion barrier is virtually unchanged (10.5 kcal mol^{-1}), while in the conformational equilibrium of the two forms the chair type predominates (40 : 60).[162] Different dibenzo-3-octanols with methyl groups in the 4-, 7-, and 8-positions also, according to the ^1H NMR spectroscopy data, prefer the TB conformation with an *a*-orientation of the hydroxyl group. Compounds that contain one methyl group each at C(4) or C(8) are conformationally heterogeneous and exist as the equilibrium mixture *a*-TB ⇋ *e*-TB (the difference in energy between these conformers is not large—0.33 and 0.44 kcal mol^{-1}.[163]). Similar behaviour is shown by dibenzocyclooctenes containing fragments such as Br and AcO.[163,164] As was indicated above, introduction of a carbonyl group into an eight-membered ring has little effect on its conformational behaviour, which is also confirmed in the case of ketone (LXIV); when R = H the equilibrium TB ⇋ C, which is usual for dibenzo derivatives, occurs, whereas when H is replaced by Me the equilibrium is displaced towards mirror-image TB conformers.[164]

Dynamic spectroscopy has been widely used to study heterocyclic analogues of the type (LXV)–(LXVII), for which the experimental results on inversion barriers have been correlated with those calculations on the transition state energies. Azocines (LXV) with X =

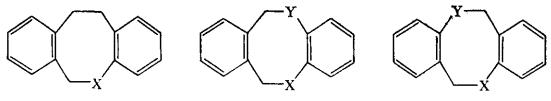
Table 5. The conformations of derivatives of 1,5-cyclooctadienes, cycloocta-trienes and -tetraenes.

Compounds	R	R	Torsion angles, deg.*								ΔE, kcal mol^{-1}	Notation**	Refs.
			1	2	3	4	5	6	7	8			
(LXI)	H	H	—	−89.8	52.5	21.8	5.3	—	—	—	—	T (C_2)	[148]
			0	6.7	−62.6	89.0	0	—	—	—	—	C (C_{2h})	[148]
			0	72.2	−100.0	72.6	0	—	—	—	—	B (C_{2v})	[148]
(LXI)	Br	H	—	−82	65	11	−1	—	—	—	—	TB (C_2)	[150]
(LX)	$OCNH_2$	Me	—	−74.9	76.0	−1.9	−3.4	—	—	—	—	TB	[151]
(LXI)	H	H	—	−86.5	63.3	8.1	6.2	—	—	—	—	TB	[149]
(LXXI)	—	—	−4	−54	−4	51	1	−12	−63	97	0	TB (C_1)	[31]
	—	—	0	64	7	−68	0	68	7	−64	4.8	B (C_s)	[31]
	—	—	−2	−12	−1	66	−114	—	—	—	6.6	HC (C_2)	[31]
(LXXV)	—	—	0	−44	87	−8	−58	—	—	—	0	TBC (C_2)	[31]
	—	—	0	84	−57	0	0	—	—	—	1.8	HC	[31]
	—	—	7	22	16	−7	−36	−4	89	−88	4.1	TS	[31]
(LXXVI)	—	—	−3.1	−63.0	−1.8	69.2	—	—	—	71.3	—	B	[174]
(LXXVI) — octamethyl	—	—	4.2	−66.3	−5.4	−61.8	5.4	—	—	78.8	—	B	[62]

* Numbering of the angles corresponds to that given in Table 1.

** TS is transition state; symmetry of the conformers is given in brackets.

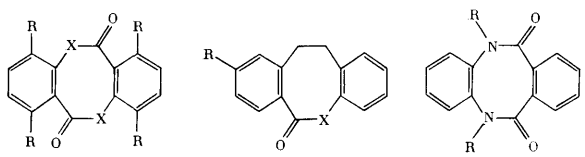
NAc, NBz, NSO_2, Ar, NCH_2Ph, and NH are characterised by an equilibrium of the C and B forms with transition barrier between them of 10.6–11.1 kcal mol^{-1} (calculated 13.2 kcal mol^{-1}); the barriers for the transitions B ⇋ B* or B ⇋ TB are much higher (14.3–20.1 kcal mol^{-1}).[160]



(LXV) (LXVI) (LXVII)

Diazocines (LXVI) and (LXVII) are also conformationally heterogeneous, but the difference in energy between the alternative C and B forms is low—less than 0.28 kcal mol^{-1} with the exception of diazocine (LXVI) for which the inversion barriers are 12.9 to 14.1 kcal mol^{-1}.[160,165] 3,8-Thiazocine (LXVI) with X = S and Y = NAc also exhibits a temperature dependence in its ^1H NMR spectra, which is due to its conformational heterogeneity. The transition barrier between its forms is substantially higher than in diazocines and amounts to 18.6 kcal mol^{-1}.[165] In contrast to diazocines, in dithiocines (LXVI) and (LXVII) with X = Y = S the conformational equilibrium C ⇋ B is displaced up to 80% towards the B conformer. In the corresponding disulphones (X = Y = SO_2) only one conformer is detected at low temperatures. The barriers for the inversion B → C in compounds (LXVI) (9.0 and 11.9 kcal mol^{-1}) for the sulphide and sulphone are substantially lower than in the corresponding (LXVII) compounds (12.4 and 18.6 kcal mol^{-1}).

When coming to consider the conformations of keto derivatives (LXVIII)–(LXX), we should remember that since the carbonyl group situated in the vicinity of the heteroatom forms a planar fragment, diketone (V) in a conformational sense behaves in a similar manner to 1,5-cyclooctadienes. In this respect diketones (LXVIII) and (LXX) can also be regarded as derivatives of cyclooctatetraene (see next Section). In fact, the conformational properties of diketones (LXVIII) with X = NH, NCH_2Ph,[166] O,[167] S[168] are controlled by a reversible equilibrium inversion of the ring between the B ⇋ B forms. The activation energy of these conformational transitions is high—in diazocines it is 27 kcal mol^{-1},[166] while in dioxocines and dithiocines it is reduced to 17.7–18.4 kcal mol^{-1} [167] and amounts to 24.6 kcal mol^{-1} when R = Me.[168] It has been confirmed by X-ray diffraction analysis of dithiosalicide (LXVIII) with R = H, X = S that the preferred conformation in this case is the boat form with a pseudoplane of symmetry passing through the centre of the S–C(O) bonds.[169]



(LXVIII) (LXIX) (LXX)

The barrier in the lactam (LXIX) with R = H, X = NCH_2Ph is also lower (21.4 kcal mol^{-1} [170] (the symmetrically substituted dilactam (LXX) is conformationally pure.[166]) There are indications that the dipole moment of lactone (LXIX) with R = Br (4.09 D) is consistent with the B conformation.

Thus, it may be seen that the conformational behaviour of derivatives of 1,5-cyclooctadienes has as yet been studied insufficiently and to a considerably lesser degree than for 1,4-cyclooctadienes.

Nevertheless, the results obtained indicate that the remote relative configuration of the two planar fragments helps to stabilise flexible (TB or B) rather than chair-like forms. Introduction of heteroatoms or keto groups into the ring produces an increase in the degree of preference for the B conformer relative to TB, which is due to their occurring in a state analogous to cyclooctatetraene systems.

VII. DERIVATIVES OF CYCLOOCTA-TRIENES AND -TETRAENES

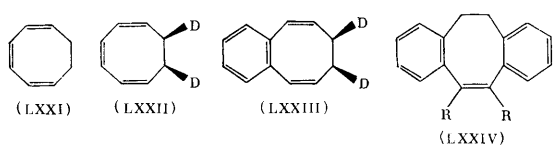
1. 1,3,5- and 1,3,6-Cyclooctatrienes

Since in 1,3,5-cyclooctatriene (LXXI) the alternation of double bonds and single bonds is conducive to conjugation, the theoretical examination of compounds of this type is based on a model of conjugated bonds, assuming a small rotation about the single C_{sp^2}–C_{sp^2} bonds.[31,171,172] It was shown that the most stable form is TB conformer in which the dihedral angle along the CH_2–CH_2 bond is equal to 63°, in contrast to the B form where it has a value of zero. The torsion angles of the three conformers, including the half-chair (HC), are listed in Table 5. The difference in energy between the TB and B forms is due to conjugation effects and torsional interactions. The results of calculations are consistent with dynamic ^1H and ^{13}C NMR spectroscopy data for (LXXI); it was found that the difference in energy between the TB conformer and the B and HC forms is 4.3 and 6.2–6.7 kcal mol^{-1}, and ring inversion occurs with a barrier of 6.6 kcal mol^{-1}.[171]



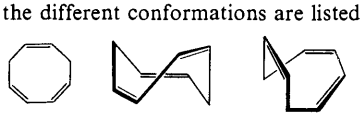
TB B HC

The introduction of benzene rings in place of double bonds increases the barriers. Thus, on going from (LXXII) to (LXXIII) it increases from 6.7 to 9.2 kcal mol^{-1},[173] and the presence of a second benzene ring contributes to a twofold increase to 18.7 kcal mol^{-1} in the dibenzo derivative, this trend being maintained in the tribenzo analogues.[173] The effect of alkyl substituents on the multiple bond in dibenzo derivatives (LXXIV) on the magnitude of the barrier was studied; in the monomethyl derivative it is higher than in the unsubstituted compound with R = R′ = H and lower than in the disubstituted compound with R = R′ = Me.[158]



(LXXI) (LXXII) (LXXIII) (LXXIV)

For 1,3,6-cyclooctatriene (LXXV) calculations have identified two energy minima, which correspond to the TBC and HC conformers with C_2 and C_s symmetry. The energy difference between them is 1.8 kcal mol^{-1} and the transition barrier 4.10 kcal mol^{-1}.[31,171] The torsion angles in the different conformations are listed in Table 5.



(LXXV) TBC HC

2. Cyclooctatetraenes

Although in 1,3,5,7-cyclooctatetraenes (LXXVI) the alternation of double and single bonds is conducive to conjugation, in a planar system strong angular and torsional interactions occur—and for that reason the B form occurs in this case as a compromise. This has been demonstrated by electron-diffraction data[174] and the results of calculations[1] for (LXXVI) and by X-ray diffraction analysis for its octamethyl derivative.[62] The torsion angles about the cyclic bonds of the B form are given in Table 5. According to the X-ray diffraction studies, introduction of substituents into the ring changes the degree of flattening in the B conformation. It is determined by the magnitude of the so-called external dihedral angles (α). Carboxy-substituted cyclooctatetraene,[175] the 1,4-dinitro derivative,[176] and the 1,3,5,7-tetramethyl derivative[177] have dihedral angles in the range 39–45°.



The proximity of the two pairs of substituents at the 1,4,5,8-positions of the ring (R = $CH_2OC_6H_4Me$-*p*) [178] causes the angle to increase to 48°. The degree of flattening of the octasubstituted compounds is determined by the steric requirements of the substituents. For fluorine atoms which are small in volume the angles are not large (α is 41.0° and 41.7°),[179] on substitution with methyl groups it increases by 8.7–11.0°,[62] and a further increase in substituent volume (phenyl groups) causes the angles to increase to 58.0° and 53.3°.[180,181] In paracyclophane systems no distinctive changes have been found,[182,184] and the conformational state of tetra-annulated systems is determined by the nature of the annulated ring. The tetracyclopentane derivative has the B form (α is 41.4° and 42.3°)[184] and the tetracyclobutane derivative has a planar structure (0.5° and 2.1°).[185]

As regards dynamics, according to the NMR spectroscopic data cyclooctatetraene and its derivatives are characterised by two processes—ring inversion and bond displacement.[186–188] The first of these processes occurs via a planar transition state of D_{4h} symmetry with localised double bonds, and the inversion barrier amounts to about 10 kcal mol^{-1},[189] while for the second process it is higher by 4 kcal mol^{-1}. It is open to question whether a planar structure of D_{8h} symmetry with equivalent C–C bonds[190,191] should also be considered, and in this connection a detailed examination of factors such as resonance destabilisation (antiaromaticity),[192] angle strain, van der Waals repulsion,[193] and related interactions[190] is required. The introduction of alkyl or aryl groups adds a chirality element, with the result that the possibility arises for isolating optically active isomers.[194–198] From the difference between the ^1H NMR spectra of the isomers it is possible to determine the degree of flattening in the ring. Thus, for derivatives with a 1,2-annulated four-six membered ring system it was shown that flattening of the cyclooctatetraene ring increases as the size of the annulated ring decreases.[199]

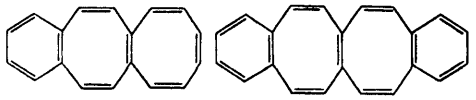
The boat conformation is preserved in mono- and di-benzo-octalenes (LXXVII) and (LXXVIII).[200,201] Such systems are of interest for studying the inversion barriers between the B and B* conformers using dynamic NMR spectroscopy. In dibenzooctalenes it is quite high (12.3 kcal mol^{-1} for (LXXVIII) with R = CH_2F [202]) and shows little dependence on the nature of R, while in dioctalenes the barrier is even higher (15.3 kcal mol^{-1} [201]). The conformational behaviour of di-, tri- and tetra-benzooctalenes is similar to that of the biphenyl derivative.[199]

The conformational situation can change, as indicated above, when heteroatoms are introduced. In fact, dibenzodiazocine (LXXX) has a distorted B form, the torsion angles of which are also listed in Table 5.

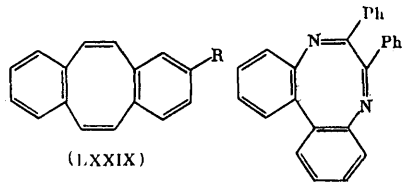
Table 6. The conformations of cyclotetraphosphazenes.

Compounds	Torsion angles, deg.								Conformations	Refs.
	1	2	3	4	5	6	7	8		
$N_4P_4Cl_4(NMe_2)_4$	38.4	49 8	29.3	67 3	31 6	25.8	67.2	46.8	BB	[207]
$N_4P_4(OMe)_8$	34	45	42	55	30	43	40	52	BB	[208]
cis-$N_4P_4F_4(NMe_2)_4$	33.5	43.8	34 7	48.7	31.6	53.3	18.8	36 6	B	[210]
$N_4P_4Ph_4(NMe_2)_4$	95	—53	—21	73	—95	53	21	—73	CC	[211]
trans-$N_4P_4Ph_4Cl_4$	75	—41	—24	62	—75	41	24	—62	CC	[212]
$N_4P_4Cl_2(NMe_2)_6$	76	—44	—19	61	—76	44	19	—61	CC	[213]
$N_4P_4Cl_6(NMe_2)_2$	77	—41	—26	65	—77	41	26	—65	CC	[214]
$N_4P_4Cl_8$	76	—45	—20	59	—76	45	20	—59	CC	[215]
trans-$N_4P_4F_4(NMe_2)_4$	66	—50	—5	40	—66	50	5	—40	CC	[216]
cis-$N_4P_4Cl_4Ph_4$	69	—43	38	—56	53	—34	40	67	CC	[217]
$N_4P_4F_7(C_5NH_6)$	14.4	—13.0	—6	5,7	3.3	4 3	—21.7	12.4	*	[218]

* Structure is almost planar.



(LXXVII) (LXXVIII)

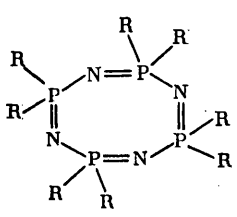


(LXXIX) (LXXX)

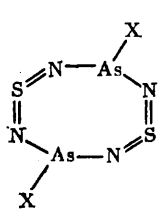
3. Inorganic 8-Membered Heterocycles with Planar Fragments

Extensive opportunities for studying the effect of geometric parameters and intramolecular electronic interactions on conformations are provided by the data on cyclotetraphosphazenes (LXXXI), where by varying the substituents on the phosphorus atom it is possible to obtain a wide variety of compounds, including geometric isomers. X-Ray diffraction studies indicate that the endocyclic PNP and NPN angles are determined to a considerable degree by the nature of the exocyclic substituents on phosphorus and can vary over a very wide range. For F-substituted compounds an almost planar structure of the P_4N_4 ring is characteristic.[204] Some of the compounds studied have a distorted saddle-shaped conformation (BB according to the terminology used in this review); these are $N_4P_4Cl_4Ph_4$,[205] $N_4P_4Cl_2(NMe_2)_6$,[206] $N_4P_4Cl_4(NMe_2)_4$,[207] N_4P_4.$(OMe)_8$.[208,209] A structure similar to the B form was found in $N_4P_4F_4(NMe_2)_4$.[210] A large proportion of the cyclotetraphosphazenes have a CC conformation in which four P atoms are situated in one plane.[211-217] In one case the CC form is stabilised with four coplanar N atoms—this is in the *cis*-isomer of $N_4P_4Cl_4Ph_4$.[217] An increase in the number of F atoms to seven helps to flatten out the ring. In the last of the examples on cyclotetraphosphazene given in Table 6 a nearly planar conformation is present, which is seen very clearly from the values of the dihedral angles.[218]

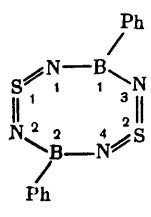
X-Ray diffraction data have been obtained for compounds that contain two adjacent diplanar fragments. The first of them (LXXXII), as for cyclotetraphosphazene, has a BB conformation in which the As atoms occupy the flagpole position and the t-butyl groups are in equatorial positions.[219] In diborocine (LXXXIII)[220] the boron atom is tending to retain a coplanar configuration for three bonds, so the conformation of the compound changes, being characterised by a bend along the line $N_1...S_2$ and by the presence of two planar groups $N_1B_1N_3S_2$ and $S_2N_4B_2N_2S_1N_1$ (the angle between these two planes is 126°).



(LXXXI)

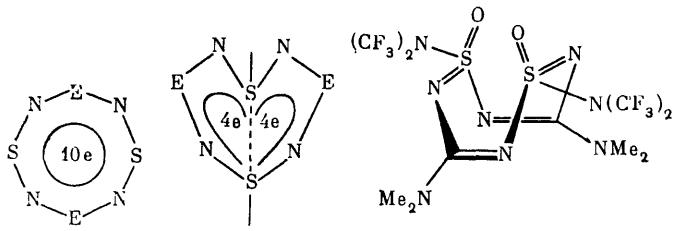


(LXXXII)



(LXXXIII)

Compounds of the type E(NSN)E with 10 π-electrons (obeying the $4n + 2$ aromaticity rule) can exist, depending on the nature of E, either in a planar form (LXXIV) with E = CPh,[221] S as in $S_4N_4^{2+}$,[222-224] $S_4N_4Cl_2$,[225] $[S_4N_4Cl]^+.X^-$ [X = $FeCl_4$,[226] $ZrCl_{10}$[227]] or in a butterfly conformation (LXXXV) with E = PMe_2,[228] $CNMe_2$ [221] and with a transannular interaction between the two sulphur atoms. At the same time in adducts of type $S_4N_4.AsF_5$ a BB (saddle) form occurs with the four sulphur atoms in one plane.[229] A deformation of the BB form to the B conformation is also possible, as is shown in the case of the dioxide (LXXXVI).[230]



(LXXXIV) (LXXXV) (LXXXVI)

- - - o 0 o - - -

It is possible to draw the following conclusions from what has been stated above. Eight-membered rings with planar fragments are conformationally mobile systems whose behaviour is closely related to the nature of the heteroatoms and the planar fragments and their relative configuration. The main and most clearly expressed trend is the tendency to adopt a chair-type conformation that corresponds the closest possible to the most stable BC form of cyclooctane. This is opposed by purely geometric limitations—the preservation of a planar configuration of the cyclic atoms that form a planar fragment and the two atoms adjacent to them. As a result, the TBC or C form occurs instead of the BC form. However, the introduction into the ring of heteroatoms capable of producing large angular deformations can contribute to inclusion in the ring also occurring in the BC form. An indication of this is the case of 1,2-cyclooctadiene and 1,5,2,4,3-dioxadiphosphazocine corresponding to it—they exist in the TC and BC forms respectively. Since the occurrence of the BC form is extremely difficult in compounds with four planar fragments, the majority of cyclotetraphosphazenes have a CC structure. 1,3-Cyclooctadienes and cyclooctatetraenes have a TBC conformation while 1,5-cyclooctadienes have the C form. The introduction of heteroatoms into the ring can lead to a greater stabilisation of the B conformer relative to the TB form. In all of the examples with diplanar fragments examined it is the B conformation that occurs in a particular proportion. In addition to heteroatoms, the nature and relative configuration of planar fragments also have a substantial effect on conformational behaviour. Changes can be seen clearly on going from rings with double bonds to benzo and naphtho derivatives; the main consequence of this transition is related to the increase in inversion barrier. It will therefore be of particular interest in the future to study heterocycles containing multiple bonds.

It can be seen from the material presented that not all types of compounds have been studied sufficiently. This must mainly concern the initial stage of the studies, when it is still premature to make far-reaching general conclusions. The most complete and interesting results have been obtained for dibenzo and dinaphtho derivatives of 1,4-cyclooctadienes, but many of them still require further tests and checks. It is still necessary to apply much effort in

order to determine all the electronic factors that govern the preference for one or other structures. Matters are much more complex than they appeared to be previously concerning compounds that contain four planar fragments and whose heterocyclic representatives all the time reveal new cases of conformational diversity. While for cyclooctatetraene it would be possible to talk about a single preferred form, namely, the boat form, in heterocyclic derivatives other structures are found that are typical, it would appear, only for saturated systems—structures such as the CC and BB forms. As can be seen, eight-membered rings with planar fragments are promising models for the development of conformational analysis as a whole. The correct analysis of compounds that are so complex in terms of conformation is possible on the basis of quantitative criteria for representing the conformations. The development of principles of conformational analysis for the class of compounds considered here will be a stage in proceeding towards saturated eight-membered rings and large-sized rings that are more complex in terms of conformation.

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Reactions of Transition Metal Polyhydride Complexes with Hydrocarbons

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The literature data on the interaction of transition metal polyhydride complexes with hydrocarbons are surveyed and analysed. Attention is concentrated on the examination of reactions with participation of the C-H bonds of hydrocarbons, i.e. on the activation of C-H bonds. The principal features of these reactions—the influence of the central atom of the complex, the nature of the stabilising ligands, the structure of the hydrocarbon, the reaction conditions, the solvent, and thermodynamic and kinetic factors—are examined. The possibility of increasing the catalytic activity of systems based on transition metal polyhydride complexes is discussed.
The bibliography includes 87 references.

CONTENTS

I. Introduction 1162
II. Interaction of transition metal polyhydride complexes with hydrocarbons 1162
III. Factors influencing the reactivity of transition metal polyhydride complexes in reactions with hydrocarbons 1171

I. INTRODUCTION

The term "activation of the C—H bond" in metal complex catalysis denotes processes in which a more reactive carbon—metal bond is formed from a C—H bond at least as an intermediate stage in some kind of process (isomerisation, isotope exchange, dehydrogenation, etc.).[1] In many compounds, the C—H bonds are sufficiently reactive to interact with the active centres of metal complexes. Many examples of reactions with participation of reactive C—H bonds, such as cyclometallation, isomerisation of olefins, isotope exchange in aromatic hydrocarbons, etc. are known.

About two decades ago, Shilov and co-workers[2] showed that in the presence of platinum(II) compounds isotope exchange takes place in solution between saturated hydrocarbons and deuterium. This discovery altered significantly the established ideas about the reactivity of alkanes and influenced greatly the further development of research into the activation of the C-H bond of hydrocarbons. However, for a long time it was impossible to discover new homogeneous systems capable of activating the C—H bonds of unstrained saturated hydrocarbons under mild conditions.

The beginning of the 1980s was marked by considerable advances in this field of research: the first examples of reactions involving the oxidative addition of saturated hydrocarbons to metal complexes with formation of stable alkyl hydride derivatives were discovered and investigated and the possibility of the selective homogeneous catalytic dehydrogenation of alkanes and cycloalkanes was demonstrated. An important step was made on the way to the creation of homogeneous catalytic systems capable of converting saturated hydrocarbons into their functional derivatives under mild conditions. The current interest in this problem is evident—after all, a considerable proportion of the organic raw material resources in fact comprise saturated hydrocarbons, whose low chemical reactivity prevents their widescale employment in chemical industry. The thermal and free-radical reactions used to synthesise functional derivatives of alkanes require a large expenditure of energy and are distinguished by a low selectivity. The need for the creation of new highly selective ways of processing hydrocarbons is the reason for the ever increasing interest in the study of the reactions of alkanes and cycloalkanes with transition metal complexes.[3,4]

Three main types of metal complex systems capable of activating the C—H bond of saturated hydrocarbons under mild homogeneous conditions are known at present—platinum(II) salts in an acid medium, biscyclopentadienyl derivatives of the lanthanides and actinides, and also transition metal polyhydride complexes and their derivatives. There exist a number of reviews on the first two types of activating systems, for example, those of Shilov and Shteinman[5] and Rothwell.[6]

The present review deals with the available literature data at the beginning of 1987 on the interaction of hydrocarbons with transition metal polyhydride complexes (PC)—compounds containing four and more hydride ligands linked to one transition metal atom. The types of PC known at present, the methods for their synthesis, and their chemical and physicochemical properties have been examined in detail in existing reviews.[7,8] The high reactivity of PC with respect to the C—H bonds is explained by the relative ease, characteristic of these compounds, with which they lose some of the ligands (the splitting off of hydrogen or phosphine). This involves the formation of coordination-unsaturated intermediates which tend to fill the coordination sphere by forming metal—hydrogen bonds and which are capable of abstracting a hydrogen atom from the molecules of compounds of different classes—alcohols, ethers, and saturated and unsaturated hydrocarbons.

The studies on the reactions of transition metal PC with hydrocarbons are developing vigorously. We therefore thought it useful to examine initially the available data, in some cases still inadequate, on the reactions of various PC with hydrocarbons and then to discuss the principal features of the processes considered and the factors influencing the reactivity of PC.

II. INTERACTION OF TRANSITION METAL POLYHYDRIDE COMPLEXES WITH HYDROCARBONS

1. Group VB Metal Complexes

The niobium pentahydride $NbH_5(DMPE)_2$, where DMPE = 1,2-bis(dimethylphosphino)ethane, forms an ethylene complex on interaction with ethylene, whereupon hydrogen and traces of ethane are evolved:

$$NbH_5(DMPE)_2 + C_2H_4 \xrightarrow[16\ h,\ 1\ atm]{pentane,\ 25\ ^\circ C} NbH(C_2H_4)_2(DMPE)_2 + 1{,}8H_2 + C_2H_6 \text{ (traces)}.$$

When the reaction is carried out with deuterioethylene (Nb : C_2D_4 = 1 : 6), isotope exchange of ethylenic and hydride hydrogen atoms is observed; the hydrogen evolved consists of a mixture of isotopes (21% H_2, 44% HD, and 35% D_2). The exchange is slow and does not lead to the broadening of the ^1H NMR signals even at 95 °C in toluene-d_8.[9] The insertion of deuterium in the alkyl groups of the phosphine ligands was not observed.

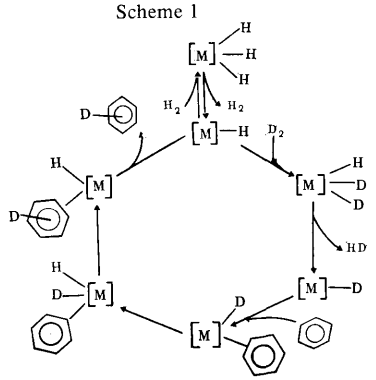
In contrast to the niobium complex, its tantalum analogue is much less reactive in relation to ethylene.[9] According to patent data, niobium and tantalum pentahydrides catalyse the dimerisation and hydrogenation of ethylene at an elevated temperature and pressure.[10]

The polyhydride complexes of the metals in the third transition row, having an odd number of valence electrons (TaH_5L_4,[11,12] ReH_7L_2,[13] ReH_5L_3, and IrH_5L_2,[14,15] where L is a tertiary organic phosphine), are active catalysts of isotope exchange between molecular hydrogen and aromatic hydrocarbons. $TaH_5(DMPE)_2$ proved to be the most active among these catalysts. The isotope exchange reaction has the following characteristic features:[12] (1) only the aromatic C–H bonds participate in the isotope exchange (in contrast to the exchange catalysed by metallic platinum or $PtCl_4^{2-}$, deuterium does not enter into the methyl groups of toluene or xylene); (2) the exchange takes place in stages—one C–H bond is involved in the exchange in each cycle of the reaction; (3) the reaction is sensitive to the steric effects of the substituents (deuterium exchange in the *ortho*-positions relative to the methyl or trifluoromethyl group takes place to an insignificant extent; the introduction of a second substituent in the *para*-position relative to the first retards the reaction sharply; electron-accepting substituents accelerate the reaction but the differences between the rates of reaction for monosubstituted arenes are small regardless of the type of substituent); (4) the presence of the isotope effect $k_H/k_D = 2-3$ shows that the C–H bond is dissociated in the rate-determining stage.

When triphenylphosphine is added to the reaction mixture, the hydrogen atoms in the *meta*- and *para*-positions in the benzene rings of phosphine participate exclusively in the isotope exchange, while in the presence of the $RuHCl(PPh_3)_2$ catalyst, the hydrogen atoms in the *ortho*-positions are exchanged. It has been suggested that, in the system considered, the phosphorus atom of triphenylphosphine is not coordinated to the tantalum atom and the polyhydride reacts with PPh_3 in the same way as with a substituted benzene having bulky PPh_2 substituents hindering the exchange in the *ortho*-position.

A mechanism has been proposed for the isotope exchange, including alternating stages involving the reductive elimination of H_2, the coordination of the arene, and oxidative addition:

Scheme 1



The weak influence of substituents is explained by the fact that both the oxidative addition and the coordination of the arene influence the rate of the reaction. It has been suggested that substituents exert the opposite influence on the rates of these stages, which in fact leads to the observed variation.

The absence of the deuteriation of the more acid hydrogen atoms in the methyl groups of toluene and anisole shows that only the hydrogen of the double bond coordinated to the metal is exchanged.[12]

The interaction of $Cp^*TaH_4L_2$ ($Cp^* = \eta^5$-C_5Me_5) with ethylene leads to a mixture of tantalum-containing products, ethane, but-1-ene, and free phosphine. Depending on the nature of the ligands L, the rate of reaction diminishes in the sequence $PMe_2Pb > PMe_3 > P(OMe)_3 > Me_2PCH_2CH_2PMe_3$, which is correlated with the decrease in the ease of elimination of the phosphine ligands from the complex. The addition of an excess of the phosphine to the reaction mixture inhibits the reaction. It has been concluded that the interaction of ethylene is preceded by the stage involving the reversible elimination of the phosphine ligand.[16] The complexes $Cp^*TaH_4L_2$, where L are monodentate ligands, form the butadiene complex $Cp^*TaCH_2CH_2CH_2CH_2(C_4H_6)$ in a high yield as a result of the reaction with ethylene. The tetrahydride stabilised by trimethylphosphine catalyses the dimerisation of ethylene to but-1-ene.

The photolysis of the benzene solution of $Cp^*TaH_4(DMPE)$ in an atmosphere of ethylene (2 atm) leads to the complex $Cp^*TaH_2 \cdot (C_2H_4)(DMPE)$ and the stoichiometric amount of ethane. When the ethylene complex is acted upon by hydrogen, the initial tetrahydride and ethane are produced.[16] The photochemical reaction probably proceeds, via a hydrogen elimination stage, in contrast to the thermal reaction.

2. Group VIB Metal Complexes

The interaction of PC of Group VIB metal complexes with hydrocarbons has been studied mainly in relation to the complexes $MH_4 \cdot (DPPE)_2$ [DPPE = 1,2-bis(diphenylphosphino)ethane] and $MH_4 \cdot (PMePh_2)_4$ (M = Mo or W). At 25 °C, the above compounds do not interact with alkenes in solution. Heating of toluene solutions of alk-1-enes and $MH_4(DPPE)_2$ to 100 °C leads to the stoichiometric reduction of the alkenes.[17,18]

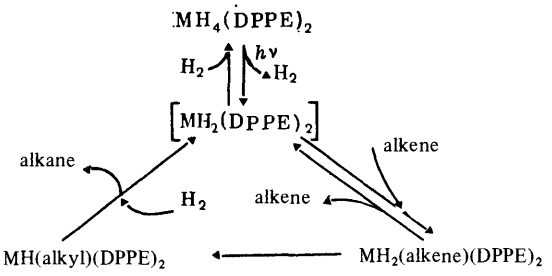
Irradiation of toluene solutions of pent-1-ene and $MH_4(DPPE)_2$ (λ = 355 nm) at room temperature leads to the stoichiometric reduction of the pentene, isomerisation with formation of pent-2-ene not being observed even after prolonged irradiation. Under analogous conditions, *cis*-pent-2-ene, 3,3-dimethylpent-1-ene, and cyclopentene are also reduced.

The photochemical reduction of $MoH_4(DPPE)_2$ with ethylene entails the formation, apart from ethane, of the diethylene complex $Mo(\eta^2$-$C_2H_4)_2(DPPE)_2$, which was isolated from the reaction mixture. The reaction with propene takes place differently and affords the π-allyl complex $MoH(\eta^3$-$C_3H_5)(DPPE)_2$.

It has been suggested that analogous products, containing η^2- or η^3-ligands depending on the structure of the initial olefin, are formed also in the interaction of $MH_4(DPPE)_2$ with other alkenes, but these products could not be isolated. The quantum yield of the pent-1-ene reduction reaction is 0.09 for $MoH_4(DPPE)_2$ and 0.006 for $WH_4(DPPE)_2$. When solutions of molybdenum (or tungsten) tetrahydride and pent-1-ene are irradiated in an atmosphere of hydrogen, the catalytic reduction of the pentene to pentane, unaccompanied by the formation of isomerisation products, is

observed (after 15 h, which corresponds to 150 catalytic cycles, only 1% of pent-2-ene is obtained). Internal olefins and olefins without an allylic hydrogen atom are reduced analogously. Photochemical reduction requires constant irradiation, i.e. long-lived catalytically active species are not formed. When a 0.1 M solution of pent-1-ene is reduced, the quantum yield is approximately equal to the yield in a stoichiometric reaction. On raising the pent-1-ene concentration to 5 M, the quantum yield also increases by an order of magnitude, which agrees with the process mechanism presented below:

Scheme 2



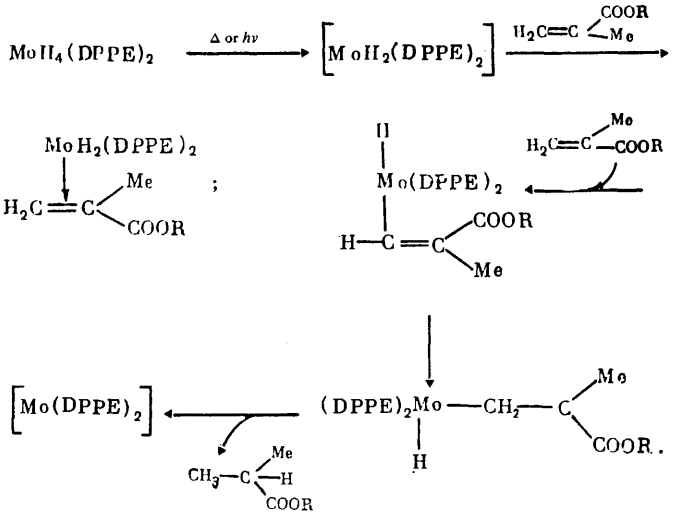
As can be seen from the Scheme, the irradiation of $MH_4(DPPE)_2$ leads to the elimination of a hydrogen molecule with formation of the dihydride, which either interacts with the alkene or again reacts with H_2.

The relative rates of photochemical reduction of alkenes correspond to those expected for reactions with participation of the sterically hindered species $MH_2(DPPE)_2$: pent-1-ene > 3,3-dimethylpent-1-ene > cyclopentene > *cis*-pent-2-ene. The hydrogenation proceeds without the isomerisation of the alkenes, in contrast to many other photocatalytic systems investigated previously.[19] In the reduction of pent-1-ene by deuterium, deuterium atoms add stereospecifically to the double bond and are not distributed statistically among various positions in the molecule, which would have been observed on isomerisation. It is believed[18] that the absence of isomerisation is associated with the steric hindrance due to the two bulky bisphosphine ligands. However, one should note that data concerning the stereospecific addition of deuterium do not agree with the authors' hypothesis of the intermediate formation of π-allyl complexes by alkenes having allylic hydrogen atoms.

The introduction of an aryl substituent into the alkene influences appreciably the composition of the reaction products. The reduction of 4-phenylbut-1-ene under the conditions indicated above also leads to the addition of deuterium in the 1,2-positions. However, this entails the formation of an appreciable amount of isomerisation products; the absence of deuterium from these products shows that structurally different photogenerated species are responsible for reduction and isomerisation.

At 80–100 °C, the complex $MoH_4(DPPE)_2$ interacts with alkyl methacrylates, forming one mole of H_2, one mole of alkyl isobutyrate, and a certain amount of the corresponding hydrido-σ-alkenyl complex $MoH[CH=C(Me)C(O)(OR)](DPPE)_2$ [R = Et, iso-Pr, Bu, or Cy (cyclohexyl); yield 15–80%]. On irradiation, the reaction takes place at room temperature resulting in the insertion of the intermediate coordination-unsaturated species in the C–H bond of the unsaturated compound:[20]

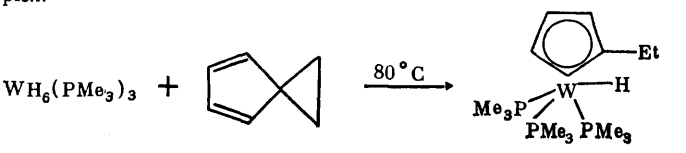
Scheme 3



Under the conditions of the photochemical reaction, molybdenum and tungsten PC are capable of interacting also with benzene and saturated hydrocarbons.[21] When solutions of MH_4L_4 in benzene-d_6 or cyclohexane-d_{12} are irradiated (254 nm), deuterium molecules are present in the gas phase after the reaction and in the case of cyclohexane-d_{12} much more deuterium is evolved than in the reaction in deuteriobenzene. The complex with methyldiphenylphosphine is much more active in this reaction than the complex with bis-(diphenylphosphino)ethane. The composition of the products of the reaction of the metal complexes and hydrocarbons has not been investigated. It has been suggested that the reaction proceeds via a stage involving the oxidative addition of a photogenerated active species to a C–H bond of the hydrocarbon. The cyclometallation reaction is a competing process, which is indicated by the appearance of deuterium in the gas phase on irradiation of $WH_4[P(CD_3)_2Ph_2]_4$ and $WH_4[P(CD_2CD_3)Ph_2]_4$ in benzene or cyclohexane.[22] The dependence of the composition of the gas phase on the irradiation wavelength (deuterium is not observed in the gas phase at λ = 366 nm) and on the nature of the phosphine ligands suggests that, with increase in the irradiation frequency, not only hydrogen but also some of the phosphine ligands are split off (see the reactions with participation of ReH_5L_3).

An interesting feature of the study of Pivovarov et al.[21] is the observation of a higher reactivity of cyclohexane compared with benzene. It may be that a change in the ligand environment and in the reaction conditions will make it possible to devise a system manifesting a still higher activity in relation to alkanes than to arenes.

The reactions of the molybdenum and tungsten hexahydrides MH_6L_3 (M = Mo or W) with hydrocarbons have been scarcely investigated. It has been reported that, when a benzene solution of $WH_6(PMe_3)_3$ is refluxed in the presence of cyclopenta-2,4-dienespirocyclopropane, the cyclopropane ring is rapidly opened, which results in the formation of an ethylcyclopentadienyltungsten complex:[23]



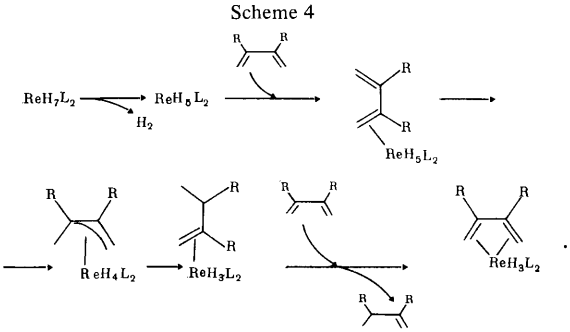
3. Rhenium Complexes

Perhaps the greatest number of different polyhydride complexes are now known for a Group VII metal—rhenium. The interaction of PC with hydrocarbons has in fact been studied in greatest detail in relation to the rhenium complexes. Technetium, an analogue of rhenium, is a radioactive element and studies on the chemical properties of technetium PC have not so far been reported.

The rhenium heptahydrides ReH_7L_2 react under mild conditions with phosphines, amines, and arsines to form the pentahydride ReH_5L_2L'. Further substitution of hydrogen, leading to trihydrides, requires much more severe conditions.[13,24] However, the interaction of ReH_7L_2 with various dienes proceeds readily under mild conditions and is accompanied by the conversion of the heptahydride into the trihydride.[25,26]

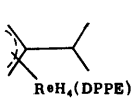
The reaction of $ReH_7(PPh_3)_2$ with buta-1,3-diene and its alkyl derivatives in boiling tetrahydrofuran (THF) ends after several minutes. The trihydrodiene complexes $ReH_3(diene)(PPh_3)_2$ are pale-yellow crystalline substances stable in air. The interaction of $ReH_7 \cdot (PPh_3)_2$ with an excess of cyclopentadiene at 25 °C results in the formation of the diene complex $(\eta^4\text{-}C_5H_6)ReH_3(PPh_3)_2$. However, with increase in the amount of the heptahydride, the complex is dehydrogenated catalytically with formation of $CpReH_2L_2$.[27] The interaction of equimolar amounts of ReH_7L_2 and cyclopentadiene in THF at 60 °C leads directly to $CpReH_2L_2$.[25] Cyclohexa-1,3-diene or cyclohexa-1,4-diene afford $(\eta^4\text{-}1,3\text{-}C_6H_8)ReH_3(PPh_3)_2$, the heating of which leads to the arene complex $ReH(\eta^6\text{-}C_6H_6)(PPh_3)_2$. Baudry et al.[26] described the following scheme for the interaction of rhenium heptahydride with dienes:

Scheme 4

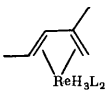


As a consequence of its low thermal stability in solution, the heptahydride loses a hydrogen molecule and is converted into the pentahydride, which interacts with the diene. The diene ligand promotes further reaction, acting as a hydrogen acceptor, and the complexes $ReH_5(\eta^2\text{-diene})L_2$ are therefore unstable and have not been isolated. The proposed mechanism is supported by the finding that only one mole of hydrogen per mole of the complex is evolved during the reaction and that part of the diene is hydrogenated to a mono-olefin.

The reaction conditions and the composition of the product depend on the properties of the ligands. Thus ReH_7(DPPE), containing the bidentate phosphine ligand, is more thermally stable and does not react with dienes under the conditions indicated. Subsequent treatment of this PC with potassium t-butoxide and dimethyl sulphate in the presence of 2,3-dimethylbutadiene yielded the first example of a PC with an allyl ligand:[28]



On refluxing in THF, the complexes ReH_7L_2 react with propene to form complexes containing the propene dimerisation product—2-methylpenta-1,3-diene—as the ligand:

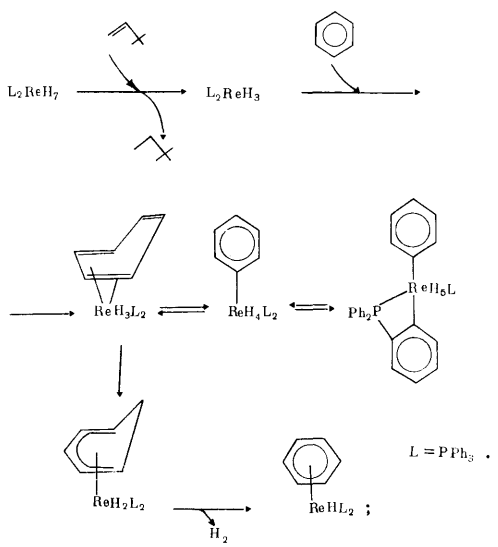


The photochemical reaction of this compound or of the initial heptahydride with an excess of propene affords $(\eta^3\text{-}C_3H_5)_2ReHL_2$, which permits the conclusion that rhenium heptahydride is successively converted initially into the diene complex $ReH_3(\eta^4\text{-}C_6H_{10})L_2$ and then into the π-allyl complex $(\eta^3\text{-}C_3H_5)_2ReHL_2$.[29]

Using the activating effect of olefins on the rhenium PC, a series of unusual reactions have been carried out.[25,26] 3,3-Dimethylbut-1-ene [t-butylethylene (TBE)], which has been shown[30] to be the most convenient dehydrogenating agent in such reactions, was used as the hydrogen acceptor.

In the presence of TBE, rhenium heptahydride reacts with benzene on refluxing, giving rise to $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$. During the reaction, one mole of H_2 is evolved and 1.1 mole of 2,2-dimethylbutane is formed. When benzene-d_6 is employed, the rhenium complex containing a 50% deuteriated cyclohexadienyl ring, 25% deuteriated hydride ligands, and triphenylphosphine ligands (deuteriated in the *ortho*-position to the extent of 10—15%) is formed. The hydrogen evolved contains hardly any deuterium. Heating of the product *in vacuo* affords the η^6-arene complex:[31]

Scheme 5



The reactions with toluene, *p*-xylene, and mesitylene proceed analogously. This results in the formation of the corresponding dihydrocyclohexadienylrhenium complexes.[32]

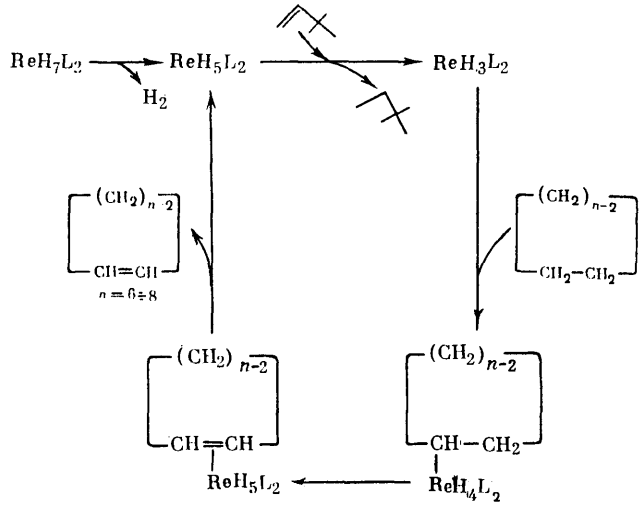
In the presence of TBE, rhenium heptahydride is capable of dehydrogenating saturated hydrocarbons—both cyclic and acyclic.[33-35] The reaction is carried out by refluxing rhenium heptahydride in the corresponding hydrocarbon in the presence of an excess of TBE in an inert atmosphere.

The reaction of ReH_7L_2 (L = PPh_3 or PEt_2Ph) with cyclopentane gives rise to $CpReH_2L_2$. The reaction terminates after 10 min, the entire hydrogen (both from the rhenium hydride and from cyclopentane) being consumed in the hydrogenation of TBE.[33]

The interaction of ReH_7L_2 with higher cycloalkane homologues (cyclohexane, cycloheptane, and cyclo-octane) leads to the corresponding cycloalkenes. It has been noted that the dehydrogenation of cycloalkanes takes place even when air or pure oxygen is passed through the reaction mixture.[34] The yield of the dehydrogenation products increases with enhancement of the electron-donating properties of the phosphine ligands forming part of the composition of the rhenium complex: $P(C_6H_4F\text{-}p)_3 < PPh_3 < P(C_6H_4Me\text{-}p)_3$.

The decrease in the ReH_7L_2 concentration from 5×10^{-2} to 3×10^{-3} M made it possible to achieve the dehydrogenation of cycloalkanes under catalytic conditions. The nature of the PR_3 ligands in ReH_7L_2 has a decisive influence on the course of the catalytic process. Best results have been obtained using $ReH_7.[P(C_6H_4F\text{-}p)_3]_2$, which reacts with cyclo-octane even at 30 °C, giving rise to 1.6 conversion cycles after 10 min. At 80 °C, nine moles of cyclo-octene are formed per mole of the PC. Cyclo-hexene may be used instead of TBE as the hydrogen acceptor in the dehydrogenation of cyclo-octane. The reaction is highly selective: no dehydrogenation products other than cycloalkenes have been observed. Rhenium heptahydrides with more electron-donating triarylphosphine ligands are less active in the catalytic process in contrast to the non-catalytic reaction. Presumably, the electron-donating substituents in the benzene ring of the ligand promote *ortho*-metallation and thereby deactivate the intermediate catalytically active species. Electron-accepting substituents hinder this reaction and therefore promote a higher yield of products. The catalytic process is described by the scheme:

Scheme 6



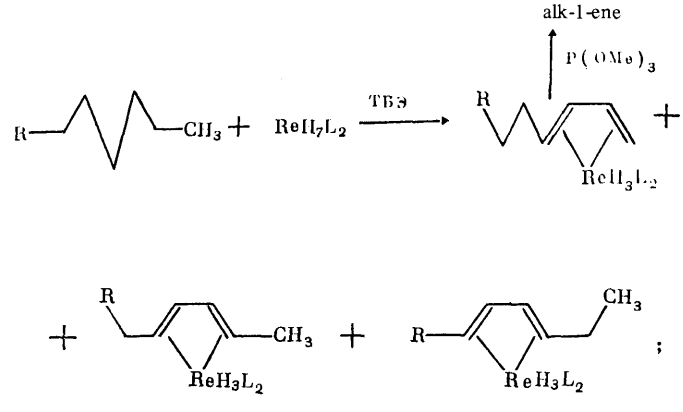
Under the conditions of this reaction, methylcyclohexane affords a mixture of isomeric olefins,[36] the thermodynamically most stable 1-methylcyclohexene being present only in trace amounts, and the main products are 3- and 4-methylcyclohexenes, which indicates the absence of radical intermediates in the dehydrogenation process. The isomeric composition of the olefins formed depends on the properties of the stabilising phosphine ligands (see Table).

The feasibility of the selective non-radical catalytic conversion of sterically unstrained saturated hydrocarbons into their functional derivatives by treatment with soluble transition metal complexes has been demonstrated[36] in relation to the catalytic dehydrogenation of cycloalkanes in the presence of rhenium hydride complexes.

Composition of the products of the dehydrogenation of methylcyclohexane catalysed by rhenium and iridium PC in the presence of an excess of TBE.[36,37]

Catalyst	Reaction conditions		Number of catalytic cycles	Reaction products, %			
				methylene-cyclohexane	methylcyclohexenes		
	T, °C	t, h			3-Me	4-Me	1-Me
$ReH_7[P(C_6H_4F\text{-}p)_3]_2$	80	1/6	3	6	29	65	1
$ReH_7(PPh_3)_2$	80	1/6	1	9	28	63	1
$ReH_7(PEt_3)_2$	80	2	0.2	28	27	45	1
$IrH_5[P(Pr\text{-}iso)_3]_2$	100	1/4	3	64	10	16	9
	100	1	3.5	55	12	18	15
	150	65	10	1	13	24	62

In the presence of TBE, rhenium heptahydrides are capable of dehydrogenating also normal alkanes.[35] Heating of ReH_7L_2 with an excess of TBE in pentane in a sealed tube (80 °C, 30 min) leads to the pentadiene complex $ReH_3(\eta^4\text{-}C_5H_8)L_2$. The yield of this complex increases on passing from L = PPh_3 to L = $P(C_6H_4Me\text{-}p)_3$. With increase in the rhenium heptahydride concentration, the yield of the complex $ReH_3(\eta^4\text{-}C_5H_8)L_2$ diminishes as a result of the competing formation of $ReH_2(\eta^5\text{-}C_5H_7)L_2$ (cf. with the results of Jones and Maguire[27]). When $ReH_3(\eta^4\text{-}C_5H_8)L_2$ is treated with trimethyl phosphite, pent-1-ene is formed in a high yield and with a high selectivity, while treatment with triethyl or triphenyl phosphite produces a mixture of pentane and pent-1-ene.[38] Treatment of the same compound with benzylisonitrile† leads to the selective formation of *cis*-pent-2-ene. Normal alkanes with 6–8 carbon atoms also react with $ReH_7(PPh_3)_2$ in the presence of TBE. This results in the formation of a mixture of isomeric trihydridodienerhenium complexes, whose treatment with trimethyl phosphite leads to alk-1-enes in a high yield and with a high selectivity:



R = H, Me, Et.

† T.Burchard and H.Felkin, New J. Chem., 1986, **10**(12), 673.

Since the isomeric rhenium complexes are in a dynamic equilibrium under the reaction conditions, the data obtained do not allow one to determine which of the C–H bonds of the alkanes is attacked in the initial stage of the process. It has been suggested that the C–H bonds of the methyl groups are the first to be attacked. In contrast to the reactions with cycloalkanes, which lead to catalytic dehydrogenation products, in the interaction of ReH_7L_2 with n-alkanes, the loss of olefins from the coordination sphere of the complex takes place to an insignificant extent, which makes it impossible to carry out the reaction under catalytic conditions.

The alkanes used in the reaction must be completely free of admixtures of olefins, because even an insignificant amount of such compounds fully inhibits the interaction of rhenium heptahydrides with alkanes.[35]

Rhenium heptahydride stabilised by tricyclohexylphosphine ligands proved to be thermally more stable‡ than the complexes with triarylphosphines, which permitted a more detailed study of certain stages of the activation of C–H bonds by rhenium PC.[39,40] At 60–80 °C, $ReH_7(PCy_3)_2$ reacts with benzene-d_6, deuterium substituting not only the hydride ligands but also the hydrogen atoms at the C(2) and C(3) carbon atoms of the cyclohexyl rings. The regioselectivity of the isotope exchange indicates an intramolecular process mechanism. The higher rate of isotope exchange at the C(3) atom agrees with the intramolecular metallation mechanism, for which the preferential formation of the less strained five-membered ring compared with the four-membered ring should be observed. Acenaphthylene $C_{12}H_8$ is hydrogenated in the inner sphere of the complex with formation of $(\eta^4\text{-}C_{12}H_{10})ReH_3L_2$. The reaction with anthracene does not occur, which indicates the ineffectiveness of the rhenium PC in radical hydrogen transfer processes leading to the hydrogenation of the 9,10-positions in anthracene.

The study of the isotope exchange between ReH_7L_2 and deuterium and of its interactions with acenaphthylene, olefins, and other compounds showed that all these reactions proceed via a stage involving the formation of the intermediate ReH_5L_2 species.

The interaction of rhenium pentahydride $ReH_5(PMe_2Ph)_3$ with hydrocarbons under the conditions of the photochemical reaction has also been investigated.[43–46] Irradiation of a solution of this complex in benzene-d_6 leads to the exchange of the solvent deuterium atoms with the hydrogen atoms in the *meta*- and *para*-positions in the benzene rings of the ligands.[43] the presence of naphthalene in the reaction mixture results in the extensive deuteriation of naphthalene, mainly in the 2,3,6,7-positions.[44]

The photochemical hydrogenation of hex-1-ene by molecular hydrogen has been achieved. The reaction is catalytic with respect to rhenium but requires constant irradiation, as in the case of molybdenum and tungsten PC: when the reaction mixture is kept in the dark for 12 h after irradiation for 10 min, there is no appreciable increase in the yield of hydrogenation products.[44]

‡ The thermal stability of rhenium heptahydrides increases with enhancement of the electron-donating properties of the ligands. Thus, $ReH_7(PMe_3)_2$, stabilised by trimethylphosphine which is a powerful electron-donating ligand with a small bulk, sublimes *in vacuo* at 40 °C and decomposes at 102 °C.[41] The conversion of ReH_7L_2 into $Re_2H_8L_4$ on heating in solution is retarded on passing from the triphenylphosphine ligand to the more electron-donating ligands PMe_2Ph and PEt_2Ph,[39] although their bulk is in fact smaller.[42] The higher stability of $ReH_7(PCy_3)_2$ can also be explained by the powerful electron-donating properties of tricyclohexylphosphine and not by its small bulk.

Reaction with internal olefins leads to the formation of hydrido-olefinrhenium complexes. When a solution of rhenium pentahydride and cyclopentene in benzene is irradiated, $(\eta^2\text{-}C_5H_8)ReH_3.(PMe_2Ph)_3$ is formed almost quantitatively. The hydrogenation of the olefin is not then observed.[44] Photolysis of the compound obtained leads to coupled hydrogenation-dehydrogenation of the coordinated olefin, which results in the formation of cyclopentane and a mixture of the complexes $CpReH_2L_2$ and $CpReH_4L$.

In the photochemical interaction of ReH_5L_3 with cyclopentadiene, the tetra-hydride complex $CpReH_4L$ (L = PMe_2Ph) was mainly formed, while the thermal interaction afforded the dihydride $CpReH_2L_2$ (L = PPh_3).[25] The interaction of ReH_5L_3 with cyclo-octatetraene under irradiation gives rise to the cyclo-octatriene complex $(\eta^4\text{-}C_8H_{10})ReH_3L_2$.[45] The same compound has been obtained on refluxing $ReH_7(PMe_2Ph)_2$ with cyclo-octa-1,5-diene in hexane, which confirms the hypothesis of the intermediate formation of ReH_5L_2 both in the photochemical activation of ReH_5L_3 and in the thermal activation of ReH_7L_2. On standing for 12 h, the compound $(\eta^4\text{-}C_8H_{10})ReH_3L_2$ is fully converted into the cyclo-octa-1,5-dienyl complex $(\eta^5\text{-}C_8H_{11})ReH_2L_2$. Cyclo-octatetraene is converted into the cyclo-octadienyl ligand regiospecifically: all three hydrogen atoms transferred from rhenium to the hydrocarbon are in the *endo*-positions relative to the rhenium atom, which indicates the intramolecular character of the process.

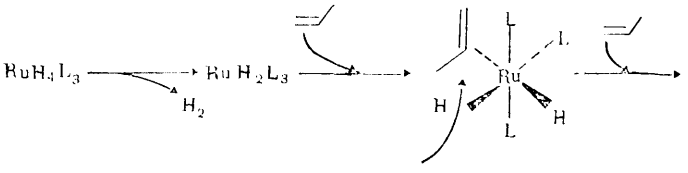
Irradiation of ReH_5L_3 in cyclopentane in the presence of TBE results in the formation of the complex $CpReH_2L_2$ in a low yield, while in the absence of TBE only the dimeric complex $Re_2H_6L_5$—the product of the interaction of ReH_5L_2 with ReH_5L_3—is formed.[47] If ReH_5L_3 (L = PMe_2Ph) is irradiated in the presence of TBE in benzene under nitrogen pressure, a mixture of products is obtained. One of them—the η^6-arene complex—contains the TBE residue, i.e. $(\eta^6\text{-}C_6H_6)ReL_2(CH_2CH_2Bu\text{-}t)$, while the other contains the *ortho*-metallated phosphine and coordinated nitrogen—$\overline{ReL_3(PMe_2C_6H_4\text{-}o)}.(N_2)$.[44]

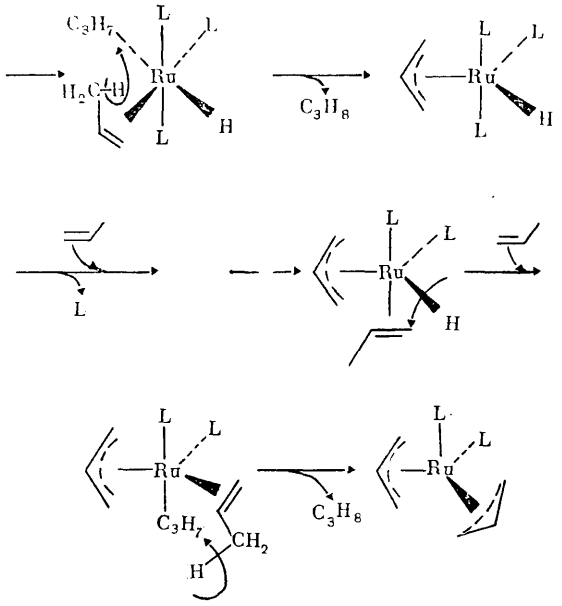
4. Iron Subgroup Metal Polyhydride Complexes

The iron tetrahydride complex $FeH_4(PEtPh_2)_3$ reacts in THF with cyclohexene, affording $FeH(C_6H_{11})(PEtPh_2)_2$ (THF). It has been suggested that an η^2-olefin iron complex is formed as an intermediate.[48]

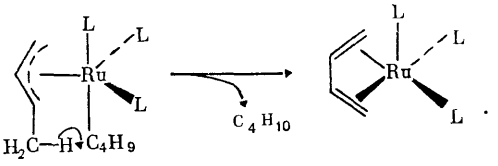
The solid ruthenium tetrahydride $RuH_4(PPh_3)_3$ catalyses the hydrogenation of ethylene but at room temperature the reaction is very slow (ten catalytic cycles in a week[49]). However, if the reaction is carried out in toluene, it is completed after 10 min with formation of $\overline{RuH(PPh_2C_6H_4\text{-}o)}(PPh_3)_2(C_2H_4)$, one mole of hydrogen and one mole of ethane being evolved.[50,51] The reaction of $RuH_4(PPh_3)_3$ with propene at 100 °C takes place in 30 min, affording bis(η^3-allyl)bis(triphenylphosphine)ruthenium:

Scheme 7





The main product of the interaction of $RuH_4(PPh_3)_3$ with an excess of but-1-ene is the butadiene complex $Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3$, the same complex being formed also in the reaction of ruthenium tetrahydride with buta-1,3-diene at room temperature. It is suggested that the butadiene ligand is formed from but-1-ene also via Scheme 7, but in the last stage the hydrogen atom is split off from the methyl group of the 1-methyl-allyl ligand:



Solutions of $RuH_4(PPh_3)_3$ in toluene catalyse the isomerisation of alk-1-enes to alk-2-enes at 25 °C.[52-54] It has been shown in relation to pent-1-ene that *trans*-pent-2-ene is formed preferentially in the isomerisation process in amounts greatly exceeding the equilibrium values for the *cis*-pent-2-ene—*trans*-pent-2-ene system. The reaction is carried out in an argon atmosphere. It takes place initially very rapidly but after a few minutes it begins to slow down and then follows first-order kinetics. The rate of reaction diminishes also when argon is replaced by nitrogen. In the first rapid stage, the isomerisation is accompanied by the hydrogenation of two moles of pent-1-ene per mole of the PC, which corresponds to the utilisation of all the hydride ligands in RuH_4L_3 and, according to the author,[54] indicates the formation of a complex of zerovalent ruthenium with the olefin. The rate of isomerisation is 250 times higher than the rate of hydrogenation. In the second stage of the reaction, only traces of pentane are formed, but, if the reaction mixture is allowed to stand for 24 h or more, yet another mole of pentane per mole of the catalyst is formed. The catalyst then loses its activity, which, however, is restored on treatment with hydrogen. The catalytic activity is apparently lost as a result of the slow *ortho*-metallation reaction.

Subsequent investigations[51] failed to confirm data indicating the formation of alkene complexes in reactions with pentenes. The product of the reaction of RuH_4L_3 with pent-1-ene is RuH_4L_4 for the stoichiometric reactant ratio. The interaction with an excess of pent-1-ene produced the diene complex $Ru(\eta^4\text{-}C_5H_8)L_3$, which is apparently formed from but-1-ene similarly to the butadiene complex. This hypothesis agrees with data demonstrating the formation of two moles of pentane per mole of the catalyst and explains the evolution of one mole of H_2 in the initial stage of the reaction.

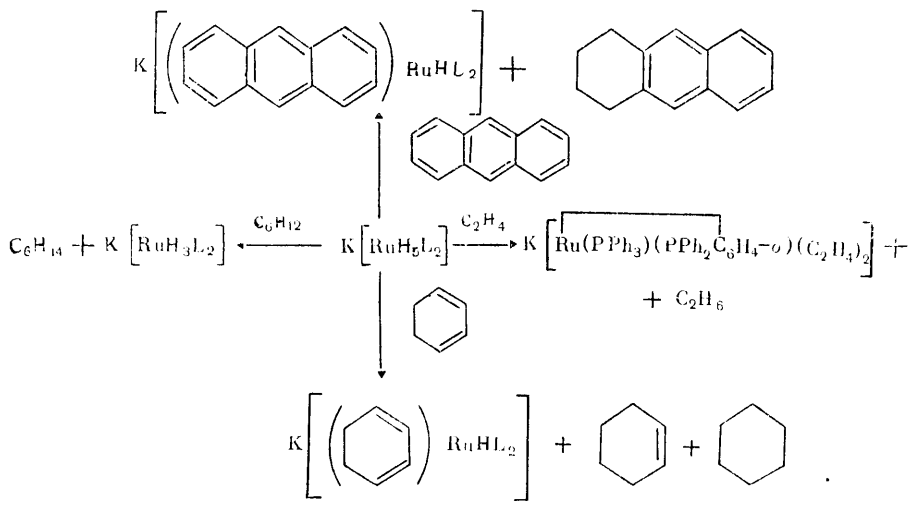
The complex $RuH_4(PPh_3)_3$ reacts with the non-conjugated chelating cyclo-octa-1,5-diene (toluene, 100 °C, 5 h) with formation of one mole of cyclo-octane and $Ru(PPh_2C_6H_4\text{-}o)(PPh_3)(\eta^5\text{-}C_8H_{11})$. RuH_4L_3 does not interact with isobutene, cyclohexene and cyclo-octene even at 100 °C.[51]

The complexes RuH_4L_3 [L = P(Pr-iso)$_3$, PCy_3, or $P(NEt_2)_3$] activate the C—H bonds of aromatic hydrocarbons and the alkyl groups in phosphine ligands at room temperature in the dark.[55,56] When the above compounds are dissolved in deuteriobenzene, a rapid disappearance of the signals of the hydride protons and the appearance of signals due to $C_6D_{6-x}H_x$ ($x > 1$) are observed. The products formed catalyse the slower deuterium exchange reaction between the solvent and the phosphine ligand. Triisopropylphosphine is deuteriated to the extent of 70—76%, tricyclohexylphosphine is 25% deuteriated and tris(diethylamino)phosphine is 40% deuteriated. The process mechanism includes stages involving the elimination of the phosphine ligand, the coordination of the arene, and the subsequent activation of the C—H bond of benzene and the phosphine ligand. Analogous reactions take place also in toluene but much more slowly. In the reaction with deuteriotoluene, an increase in temperature to 110 °C results in a sharp acceleration of the process, which indicates a change in the reaction mechanism. According to the authors,[55,56] solutions of ruthenium tetrahydride in aromatic solvents constitute the first example of a system capable of catalysing spontaneously (in the dark without heating or irradiation) the deuterium exchange between the hydrogen atoms of the phosphine ligands and the deuterium atoms of the solvent. Ruthenium polyhydride complexes are apparently much more active catalysts of the activation of the C—H bonds in arenes than the PC of 5*d* metals (tantalum, rhenium, and iridium) investigated previously.[12]

In the presence of TBE, ruthenium tetrahydrides catalyse the dehydrogenation of cyclo-octane. When $RuH_4[P(C_6H_4F\text{-}p)_3]_3$ is heated in cyclo-octane to 150 °C in the presence of TBE, 45—55 moles of cyclo-octene are formed per mole of the catalyst. The complex of ruthenium tetrahydride with triphenylphosphine ligands is less active in this reaction.[57]

The anionic ruthenium complex $K[RuH_5(PPh_3)_2]$ hydrogenates alkenes (ethylene, hex-1-ene), dienes (cyclohexa-1,3-diene), and anthracene (Scheme 8) at room temperature. Two hydride ligands participate in the reaction with hex-1-ene, four hydride ligands are involved in the reaction with cyclohexa-1,3-diene, and six hydride ligands react with ethylene, one of them being formed as a result of the *ortho*-metallation reaction. Anthracene may be hydrogenated under catalytic conditions, whereupon 1,2,3,4-tetra-hydroanthracene is formed with a high selectivity[58,59] (Scheme 8).

Scheme 8



The interaction of $RuH_6(PCy_3)_2$ with ethylene at room temperature leads to $Ru\overline{H[C_6H_{10}PCy_2]}(PCy_3)(C_2H_4)_2$. It has been suggested that the hydride ligands are displaced by the excess ethylene and that intramolecular metallation of one of the cyclohexyl groups takes place in the unstable zerovalent ruthenium complex $Ru(C_2H_4)_2 \cdot (PCy_3)_2$ formed.[56]

The reaction of $RuH_6(PCy_3)_2$ with an excess of cyclopentene in pentane at room temperature affords a mixture of the products $RuH_2(PCy_3)_2(C_5H_6)$ and $RuH(PCy_3)_2Cp$. $RuH(PCy_3)_2Cp$ is formed quantitatively in the presence of TBE. At 120 °C in the presence of TBE, ruthenium hexahydride reacts with cyclopentane to form hydridocyclopentadienyl complexes, which, however, could not be identified.[60]

Osmium tetrahydrides are much less active in relation to olefins than their ruthenium analogues.[61] The interaction of $OsH_4 \cdot (PEt_2Ph)_3$ with four moles of cyclo-octa-1,5-diene (COD) (toluene, 100 °C, 65 h) produces, after treatment with ethanol, cyclo-octene (50 % yield), the unreacted cyclo-octadiene, and $Os(COD)(PEt_2Ph)_3 \cdot EtOH$. The reaction with 12 moles of oct-1-ene under the same conditions gives rise to two moles of octane, a mixture of various octenes (isomerisation products), and an uncharacterised olefin complex of osmium. The catalytic hydrogenation of oct-1-ene, accompanied by the formation of isomerisation products, takes place in the presence of hydrogen. At the end of the reaction, the osmium PC can be regenerated from the reaction mixture. The selectivity of the hydrogenation and isomerisation of olefins has been noted: predominantly terminal alkenes are hydrogenated, while isomerisation leads mainly to internal olefins.

The irradiation of $OsH_4(PMe_2Ph)_3$ in benzene-d_6 leads to isotope exchange. After irradiation for 1 h, the initial tetrahydride is 90% converted into the deuteride $OsD_4(PMe_2Ph)_3$.[62]

It has been noted that the hexahydrides OsH_6L_2 dehydrogenate saturated hydrocarbons in the presence of TBE.[63]

5. Iridium Complexes

Like other PC of metals with an odd number of valence electrons (see subsection 1), the complexes IrH_5L_2 catalyse the deuterium exchange between gaseous deuterium and aromatic hydrocarbons.[14,15]

The iridium pentahydrides IrH_5L_2 interact with alkenes similarly to ruthenium tetrahydride: the reaction with ethylene at 45 °C in benzene affords ethane and complexes with metallated phosphines, while the reaction with propene gives rise to the π-allyl complexes $Ir(\eta^3\text{-}C_3H_5)L_2$.[64]

In the reactions with linear mono-olefins C_nH_{2n} ($n > 3$), iridium pentahydrides catalyse the intermolecular transfer of hydrogen atoms with formation of the corresponding alkane and diene. Ethylene, may be used as the hydrogen acceptor, which is reduced to ethane; a higher olefin is converted to a diene under these conditions:

$$\text{Alkene(1)} + \text{alkene(2)} \xrightarrow[2\text{-}25 \text{ cat. cycles}]{25\text{-}130\ ^\circ\text{C},\ 3\text{-}40\ \text{h}} \text{alkane(1)} + \text{diene(2)}.$$

The linear conjugated dienes formed have predominantly the *trans,trans*-configuration. The interaction of IrH_5L_2 with *cis*-but-2-ene at 60 °C yielded the butadiene complexes $IrH(\eta^4\text{-}C_4H_6)L_2$; after the reactions with pent-1-ene, hex-1-ene, and hex-2-ene, it was not possible to isolate any hydride or olefin complexes. A decrease in the catalytic activity of IrH_5L_2 is observed during the reaction. Depending on the nature of the ligands L, the catalytic activity of iridium pentahydride diminishes in the sequence $IrH_5[P(Pr\text{-}iso)_3]_2$ » $IrH_5(PPh_3)_2$ > $IrH_5(PMe_3)_2$ » $IrH_5(PCy_3)_2$.[64] The mechanism of the disproportionation reaction is probably similar to that described above for the interaction of ruthenium tetrahydride with olefins (see Scheme 7). The possibility of carrying out the reaction under catalytic conditions indicates the great lability of the coordination sphere of iridium complexes, because the reactions involving ruthenium stop

at the stage in which stable diene complexes are formed, while in the case of iridium the diene ligand is displaced from the coordination sphere by the alkene.

At 35 °C, $IrH_5[P(Pr\text{-}iso)_3]_2$ catalyses the deuterium exchange between the vinyl hydrogen atoms of TBE and the deuterium atoms of deuteriobenzene.[65] The rate of exchange of hydrogen atoms in the *trans*-positions relative to the t-butyl group is approximately an order of magnitude higher than for the *cis*-atoms. These results show that the activation of the vinyl C–H bonds can occur for certain types of olefins at a higher rate than the reaction involving the addition-elimination of the metal hydride at the double bond. The competition between the processes involving oxidative addition to the C–H bond and the formation of a π-complex has also been observed in the reaction of ethylene with the pentamethylcyclopentadienyliridium complex $[Cp^*Ir(PMe_3)]$.[66]

At a higher temperature, $IrH_5[P(Pr\text{-}iso)_3]_2$ catalyses the deuterium exchange between the hydrogen atoms of methane and the deuterium atoms of deuteriobenzene in the presence of two equivalents of TBE. Approximately 13 catalytic cycles take place after 7 days and approximately 40 cycles take place after 53 days at 80 °C. The main reaction product is CH_3D. It has been noted[67] that, in contrast to isotope exchange catalysed by transition metal halides in an acid medium,[5] in the system considered the contribution of multiple exchange is insignificant. In the absence of TBE, the deuterium exchange takes place between deuteriobenzene and the hydride ligands and also the hydrogen atoms of the phosphine ligands. An excess of TBE (> 10 equivalents) prevents the deuterium exchange with methane. In this case, small amounts of ethane, toluene, biphenyl, and propane were detected among the reaction products. It has been suggested that the first three products are formed via the reductive elimination of R–R′ from the intermediate LL′IrRR′ [R = Me, R′ = Ph, L = $P(Pr\text{-}iso)_3$, L′ = $P(Pr\text{-}iso)_2CHMeCH_2$)]. Propane is formed as a result of the degradation of the phosphine ligand.[67]

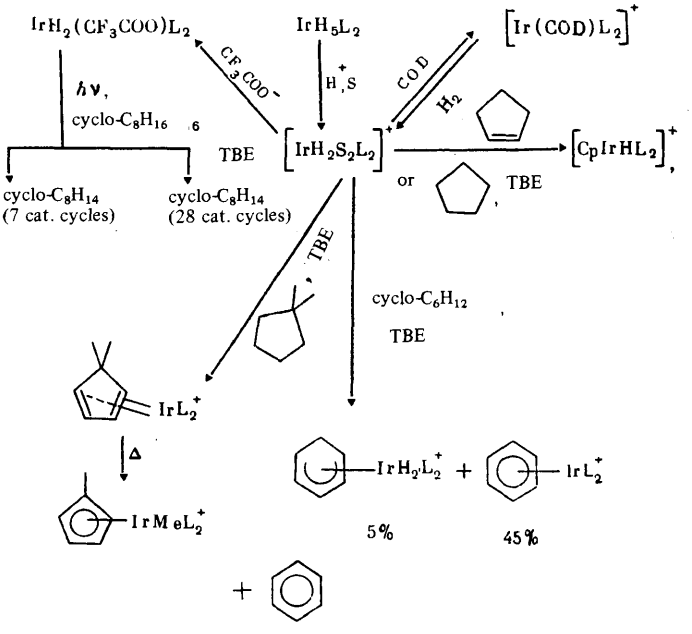
Iridium pentahydride exhibits a higher catalytic activity in catalytic reactions involving the dehydrogenation of cycloalkanes to cycloalkenes than the rhenium or ruthenium PC. Heating of $IrH_5[P(Pr\text{-}iso)_3]_2$ with an excess of TBE in cyclo-octane at 150 °C for 5 days leads to 70 moles of cyclo-octene per mole of the PC, while the best result for ruthenium tetrahydride was 45–55 moles after 10 days and that for rhenium heptahydride was 9 moles. It has been noted that compounds capable of forming 14-electron intermediates on elimination of two molecules of hydrogen, like the iridium PC, are effective catalysts of processes leading to the activation of C–H bonds in hydrocarbons.[57]

In the dehydrogenation of methylcyclohexane under the influence of $IrH_5(PPr^i_3)_2$, the main primary reaction product is methylenecyclohexane, which gradually isomerises under the reaction conditions, affording the thermodynamically more stable 1-methylcyclohexene (see Table). Iridium pentahydrides are capable of dehydrogenating catalytically not only cycloalkanes but also n-alkanes, in contrast to the rhenium PC, which forms stable diene complexes in their reactions with alkanes. The primary product of the reaction of IrH_5L_2 with n-hexane is hex-1-ene (45 °C, 5 min, 0.3 of a catalytic cycle, selectivity 78%), which isomerises rapidly, giving rise to a mixture of *cis*- and *trans*-hex-2-enes (80 °C, 30 min, 9 catalytic cycles, selectivity 75%).

The reactivity of the test systems in relation to different types of C–H bonds has been determined by the method of competing reactions: CH_2 (in cyclohexane) : CH_3 (in methylcyclohexane) : CH_3 (in n-hexane) = 1 : 8 : 60. Despite the fact that the primary C–H bonds are much stronger than the secondary and tertiary bonds, when IrH_5L_2 is used the methyl groups are in fact attacked preferentially probably under the influence of steric factors. Thus the iridium PC catalyse the selective catalytic introduction of functional groups into saturated hydrocarbons. After active and stably operating catalysts have been created, such a process might be useful, for example, for the selective preparation of functional derivatives of higher n-alkanes containing many identical methylene groups but only two methyl groups.[37,63,68]

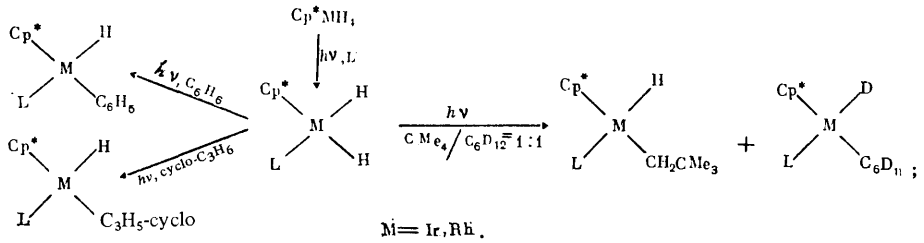
In an acid medium, $IrH_5(PPh_3)_2$ catalyses the ionic hydrogenation of olefins, surpassing in its activity systems such as $PtL_2(CF_3COO)_2$ and $Ru(CF_3COO)_3$ in CF_3COOH.[69,70] On treatment with acids, iridium pentahydrides form the complexes $[IrH_2(Solv)_2L_2]^{x+}$, where Solv is the solvating solvent (acetone, methylene chloride, etc.), an acid anion, H_2 molecule, etc., capable of entering into the C–H bond activation reactions. Like the Cp^*IrH_4 derivatives examined below, these compounds are not polyhydrides but they can be regarded as derivatives of the corresponding PC. In the present review, the properties of these compounds are examined only in terms of the aspects which are necessary for the discussion of the reactivities of the PC. We may note that it was in fact in the study of the interaction of $[IrH_2(Solv)_2L_2]BF_4$ (Solv = acetone, L = PPh_3) with cycloalkanes (cyclopentane, cycloheptane, and cyclooctane) in dichloroethane that the first stable organometallic compounds, with ligands formed as a result of the reactions of a saturated hydrocarbon in the coordination sphere of the complex, were obtained.[71] The results of a study of the reactions of these complexes with hydrocarbons[71–75] are presented in Scheme 9:

Scheme 9



Irradiation of the polyhydride complex Cp^*IrH_4 (Cp^* = C_5Me_5) in the presence of trimethylphosphine leads to the dihydride complex $Cp^*Ir(PMe_3)H_2$ capable of interacting photochemically with a wide variety of hydrocarbons—alkanes, cycloalkanes, alkenes, and arenes—to form the products resulting from insertion in a C–H bond (Scheme 10).[76,78]

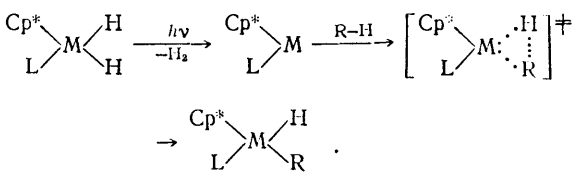
Scheme 10



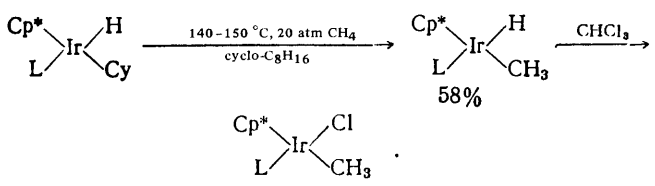
M = Ir, Rh.

The rhodium analogue $Cp^*Rh(PMe_3)H_2$ also has analogous properties. The product of the interaction of the rhodium complex with cyclopropane has been isolated in the form of the bromo-derivative which has been characterised by X-ray diffraction.[78] The study of the selectivities of the iridium and rhodium complexes examined in relation to different types of C–H bonds in saturated hydrocarbons showed that the insertion takes place predominantly in primary C–H bonds. The secondary C–H bonds are less active and the products of insertion in tertiary C–H bonds have not been observed.

Irradiation of the iridium complex in a mixture of neopentane and cyclohexane-d_{12} leads to the formation of the hydridoneopentyl and deuteridocyclohexyl complexes. These data, together with the study of the selectivity of the insertion reaction, led the authors to the conclusion that the reaction proceeds via a mechanism involving direct insertion in a C–H bond and not via a free radical formation stage:



Alkyl hydride complexes with secondary alkyl groups are thermally less stable than those with primary alkyl radicals, regenerating the reactive intermediate on heating, which leads to the possibility of the thermal activation of alkanes. At an elevated temperature, alkyliridium hydrides are capable of entering into the oxidative addition reaction with methane. The methyliridium complex formed under these conditions has been isolated on a preparative scale in the form of the chloro-derivative:[78]



III. FACTORS INFLUENCING THE REACTIVITY OF TRANSITION METAL POLYHYDRIDE COMPLEXES IN REACTIONS WITH HYDROCARBONS

The data examined shows that the transition metal PC are capable of entering into a wide variety of reactions with hydrocarbons: of forming π-complexes with unsaturated compounds, of hydrogenating, dehydrogenating, and isomerising olefins, of catalysing hydrogen isotope exchange, dimerisation, and polymerisation reactions, of dehydrogenating alkanes and cycloalkanes, etc. Involvement in coupled hydrogenation-dehydrogenation reactions is characteristic of transition metal PC, which makes it possible to carry out such reactions under conditions catalytic with respect to the PC. The formation of π-complexes by metal polyhydrides with unsaturated compounds promotes in many instances the occurrence of further reactions of the latter.

In most cases the reactions of metal PC with hydrocarbons proceed via a stage involving the C–H bonds of the hydrocarbons. For olefins, such reactions lead to the isomerisation or dehydrogenation of the initial compound, which results in an increase of the strength of the bond between the hydrocarbon ligand and the metal ($\eta^2 \rightarrow \eta^3 \rightarrow \eta^4$, etc.). It has been shown recently that a C–H bond in olefins can be dissociated via the oxidative addition mechanism and that the formation of a π-complex is in this case a competing process. The activation of the C–H bonds of arenes or alkanes by metal polyhydrides also takes place via the stage involving the oxidative addition of the hydrocarbon to the metal complex. The relative reactivities of the C–H bonds in alkanes in oxidative addition (primary > secondary > tertiary) form a sequence which is the opposite of that for the free-radical reactions. Whereas in radical processes the dissociation of the weakest tertiary bond is energetically preferable, in oxidative addition reactions, thermodynamic and kinetic factors (the stronger the metal–primary alkyl bond, the smaller steric hindrance to attack on the primary carbon atom) favour the insertion of metal polyhydrides in a primary C–H bond. The characteristics of the oxidative addition of the C–H bonds of hydrocarbons to metal complexes are being at present vigorously investigated.

It is noteworthy that metal polyhydride complexes as such are relatively inactive in reactions with hydrocarbons, because the majority of PC are electron-saturated stable compounds obeying the effective atomic number rule.[7,8] In order to involve these compounds in the reaction, a definite influence is necessary—thermal, photochemical, or chemical (for example, by a hydride ligand acceptor—a proton, a carbonium ion, or an olefin), leading to the loss of some of the hydride or phosphine ligands and the formation of highly reactive electron- and coordination-unsaturated intermediates. The molecular hydrogen or the free phosphine formed in this process can inhibit further reaction. Therefore, substitution of some of the hydride ligands in the PC can also increase the reactivity, as shown in relation to the iridium complex Cp^*IrH_4.[78,79]§

§ A series of previously unknown transition metal PC with cyclopentadienyl and alkylcyclopentadienyl ligands $CpMH_mL_n$ (M = Ta, W, Re, or Ir), whose chemical properties have been studied inadequately, have been synthesised in recent years. However, studies by Bergman[78] and Jones[79] have shown that compounds of this type merit very close attention as starting materials for the creation of systems activating C–H bonds.

Compounds formed on protolysis of certain PC are highly reactive in reactions with hydrocarbons. These are complexes in which coordination sites liberated as a result of the loss of hydride ligands are occupied by molecules (acetone, dichloromethane, etc.—solvento-complexes) or anions weakly bound to the central atom.[80]

It is noteworthy that the protolysis of transition metal PC can lead to the formation of compounds with molecular hydrogen as the ligand (hydrogen complexes). For example, on treatment with acids, IrH_5L_2 is converted under certain conditions into $[IrH_2(H_2)_2.$ $.L_2]^+$.[81] Transition metal complexes of molecular hydrogen as the ligand were first described in 1980.[82] It has been suggested that compounds of this type are more common than is known at the present time. One of the most active compounds in C—H bond activation reactions, namely ReH_7L_2, is also a complex of molecular hydrogen—$ReH_5(H_2)L_2$.[83] Molecular hydrogen complexes can probably play an important role in reactions leading to the activation of C—H bonds.[83]

The 16-electron intermediates formed on thermal or photochemical treatment exhibit a high reactivity and rapidly enter into intramolecular and intermolecular reactions. However, the formation of 14-electron intermediates is necessary for the catalytic process, which can be achieved, for example, by specially selecting hydrogen acceptors. An effective hydrogen acceptor in reactions with transition metal PC is TBE.[30] This olefin is fairly reactive, has a high heat of hydrogenation, and the 2,2-dimethylbutane formed when it is reduced is readily split off, liberating a coordination site, as a result of which a 14-electron intermediate is produced. The use of TBE made it possible to carry out the dehydrogenation reactions of cyclic and acyclic alkanes, which are catalytic as regards the PC. The dehydrogenation of an alkane to the alkene with liberation of hydrogen is an endothermic process ($\Delta H \simeq 140$ kJ mol^{-1}). Under normal conditions, the equilibrium is almost wholly displaced towards the formation of the alkane. The coupled TBE hydrogenation reaction compensates for the energy expenditure and the dehydrogenation of the alkane becomes thermodynamically feasible. However, for industrial processes involving the synthesis of functional derivatives from alkanes, reagents more readily available than TBE (for example, oxygen), interaction with which would compensate for the energy expended on the dissociation of the C—H bond, are necessary. It has not yet been possible to achieve such processes. Photochemical dehydrogenation, in which the driving force of the process would be ensured by supplying energy from outside in the form of radiation, is attractive from the technological point of view. The possibility of such a process¶ has been demonstrated in relation to the homogeneous catalytic dehydrogenation of cyclooctane by an iridium complex under irradiation.[75]

The nature of the central atom has a marked influence on the reactivity of PC. The PC of 5*d* metals are the most stable and their involvement in reactions with hydrocarbons requires comparatively severe conditions. The PC of 4*d* metals are much more reactive. Since the PC of 3*d* metals have been studied inadequately, it is impossible to compare their properties with those of other PC.

The results of the investigation of the PC-catalysed isotope exchange of deuterium with arenes have shown that compounds of 5*d* metals, having an odd number of valence electrons, are much more reactive than complexes of metals with an even number of valence electrons. The coordination sphere of the former is probably more labile, its lability increasing along the Period from left to right (cf. the reactions of rhenium and iridium PC with alkenes[35,64] and alkanes[38,68]). According to the data available at the present time, Group VIII metal compounds with an odd number of valence electrons (rhodium and iridium) do in fact have the highest activity in reactions including a stage involving oxidative addition with participation of a C—H bond.

Many transition metal PC contain tertiary organic phosphines as ligands, whose electronic and steric properties have a decisive influence on the reactivity of the PC. An increase in the number of phosphine ligands increases the strength of the metal—hydrogen bond, as a result of which more severe conditions are required for the involvement of the PC in the reaction. The role of steric factors also becomes more pronounced under these conditions. For complexes of a specific type (for example, MH_4L_4), the lability of the metal—phosphorus bond increases with increase in the bulk of the ligands.[85] The use of very bulky ligands such as PCy_3 and P(Pr-iso-)$_3$ ($\theta = 160-180°$ [42]) can be regarded as one of the methods for increasing the reactivity of the complexes. Electron-deficient complexes containing such bulky ligands and exhibiting a high reactivity in reactions with small molecules have been obtained.[86] As the electron-donating properties of the ligand become more pronounced, the thermal stability of the PC increases but so also does the reactivity of the intermediates formed both in reactions with hydrocarbons and in intramolecular processes, leading to their deactivation. One of these processes is cyclometallation for the suppression of which one uses ligands with a comparatively low reactivity in this reaction—trimethylphosphine and the pentamethylcyclopentadienyl anion. However, the best result is not always achieved by using these ligands. Thus the highest reactivity in the catalytic dehydrogenation of cycloalkanes has been observed for the iridium complex with triisopropylphosphine and not with trimethylphosphine.[57] The ratio of the rates of the target and side processes apparently depends not only on the electronic but also on the steric properties of the ligand and on the nature of the complex-forming metal. The data available at the present time are insufficient to make a well-founded choice of the metal, stabilising ligands, and the type of complex for the attainment of the best result in the reactions considered.

The properties of the solvent and the purity of the reactants play an important role in the reactions of transition metal PC with hydrocarbons. For example, the dehydrogenation of n-alkanes by rhenium heptahydrides and of cycloalkanes by solvento-complexes of iridium is suppressed by unsaturated compounds or solvents capable of forming stable complexes with the intermediate. Stable complexes of transition metals with saturated hydrocarbons are at present unknown. Unstable complexes, for example, $Cr(CO)_5.$ $.(C_6H_{12}$-cyclo), have been obtained.[87] An excess of the alkane or perfluorohydrocarbons are therefore used as solvents for the reactions of PC with alkanes. However, the question of which compounds are capable of inhibiting the reactions of PC with alkanes has not yet been solved. In certain cases, the PC interact with saturated hydrocarbons also in the presence of reactive compounds. Thus iridium complexes solvated by the highly reactive acetone dehydrogenate cycloalkanes in solvents such as chlorinated hydrocarbons, while the complexes ReH_7L_2 are capable of dehydrogenating cycloalkanes even in air. All this gives rise to the hope that

¶ In our country, studies on the introduction of functional groups into alkanes in the presence of transition metal complexes under the influence of radiation are being prosecuted by Shilov and co-workers.[84]

further investigations will create catalytic systems for the activation of alkanes which operate successfully in the usual solvents and which do not impose extremely rigorous conditions on the purity of the reactants.

Thus the results of the study of the interaction of transition metal PC with hydrocarbons have made a definite contribution to the investigation of the homogeneous activation of the C–H bonds of hydrocarbons. However, the creation of industrial methods for the selective synthesis of functional derivatives from alkanes still requires a large amount of fundamental research. It may be hoped that further investigations of the reactions of transition metal PC with hydrocarbons will prove useful for the solution of this problem, which is important from both theoretical and practical points of view.

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Agostic Hydrogen Atoms in Transition Metal Complexes

A.G.Ginzburg

The methods of formation, the structures in the crystal and in solutions, the properties, and the reactions of complexes with a bridging hydrogen atom and three-centre M...H-C bonds in which the electrons of the C-H bonds play the role of two-electron ligands at the metal atom are examined.
The bibliography includes 221 references.

CONTENTS

I. Introduction 1175
II. Early studies 1176
III. Methods of formation 1176
IV. The structure in the crystal according to data obtained by structural methods 1179
V. The structure in solutions 1183
VI. Properties and reactivity 1186

I. INTRODUCTION

The following types of binding of hydrogen have been known until recently in the chemistry of transition metal hydride complexes (see the relevant reviews[1-7]): (1) terminal hydrido-ligands in the complexes $LnMH_x$ ($x = 1-9$); (2) bridging μ^2-H ligands in the dinuclear and polynuclear complexes $L_nM(\mu^2\text{-}H)_xML_n$ ($x = 1-4$); (3) triply bridging μ^3-H ligands where the μ^3-hydrogen atom is located above the triangular face of the polyhedron (which is characteristic of the chemistry of clusters). In the FeH_6^{4-} anion, the Fe atom is in the centre of an octahedron made up of six H atoms.[8] A whole series of clusters have been obtained where 1-3 hydrogen atoms are located within a skeleton made up of metal atoms [the so called "inner cavity" or "encapsulated" ("interstitial") hydrido-ligands], for example, in the anions $HCo_6(CO)_{15}^-$, $H_2Ni_{12}(CO)_{21}^{2-}$, etc. (see the relevant reviews[6,7]).

The aliphatic C-H bonds in the molecules of CH_4 and other alkanes have been regarded traditionally as chemically inert and incapable of interacting with the metal centre in organometallic complexes. However, during the last 8-10 years fairly numerous examples of the activation of C-H bonds and of the oxidative addition to low-valence rhodium and iridium complexes have been found; numerous instances of the coordination of aliphatic and aromatic C-H bonds to transition metals have been observed and complexes with an H_2 molecules as the η^2-ligand have been obtained. The interest in compounds where the C-H bond is coordinated to a metal is indissolubly linked to the problem of the search for new effective catalysts for the activation of C-H bonds and organic synthesis on the basis of alkanes. This problem has attracted much attention and is being very vigorously investigated (see the relevant reviews[9-11]). Studies on these lines have been stimulated by advances in the field of both stoichiometric organometallic synthesis and in metal complex catalysis. These reviews consider complexes where hydrogen constitutes a bridge between the metal and carbon atoms with formation of two-electron, three-centre (2e, 3c) bonds M...H-C (CHB).† In such complexes, there is a new type of binding of hydrogen to transition metals. CHB of virtually all Group III-VIII transition metals, except vanadium and nickel,‡ have now been obtained and characterised by structural methods in the solid phase or by NMR methods in solutions. The formation of CHB proved to be characteristic not only of electron-deficient complexes of the elements at the beginning of the Periods (Sc, Y; Ti, Zr, Hf; Nb, Ta) but also of the lanthanides (Nd, Sm, Yb) and the elements in the middle of the Periods (Cr, Mo, W; Mn; Fe, Ru, Os; Co, Rh, Ir). Thus the ability to stabilise the electron-deficient centre by means of intramolecular coordination via C-H bonds, leading to the formation of a bridged M...H-C fragment, is a general property characteristic of the majority of transition metals. This phenomenon is apparently more general than was supposed previously. CHB formed with participation of aliphatic, olefinic, alkylidene (carbene), and aromatic C-H bonds are known.

All the CHB known at the present time are electron-deficient complexes whose metal centre formally has 12-16 electrons. The majority of CHB are cationic complexes or neutral molecules. The "driving force" and cause of the coordination of C-H bonds to the metal is the tendency to build up the electronic environment of the metal by means of the electron pair of the C-H bond to 18 electrons, or to decrease the electron deficiency by two electrons by increasing the number of electrons from 12 to 14 or from 14 to 16. The presence of an electron-deficient centre is an essential but not a sufficient condition for the formation of CHB. Apart from the electron deficiency, it is also necessary that the lowest unoccupied molecular orbital (LUMO) of the complex, used for the coordination with the C-H bond, should have the appropriate orientation in space. According to the results of X-ray diffraction analysis (XRD), in the case of the 16-electron complex $(\eta^7\text{-}C_7H_7)Ti(Dmpe).CH_2CH_3$,§ Ti...H-C bonds with the hydrogen of the CH_3 moiety of the ethyl group are not formed.[12] Quantum-chemical calculation has shown that in this case the LUMO consists mainly of the d_{z^2} orbital of titanium and is oriented along the z azis; owing to its unfavourable steric disposition, this orbital is incapable of effective overlap with the α- or β-CH bonds of the ethyl group and a bridge

†Complexes with hydrogen bridges. The corresponding Russian abbreviation is KMB (Translator).

‡According to the literature data for the period including December 1987, using also individual studies in 1988.

§Dmpe = $Me_2PCH_2CH_2PMe_2$.

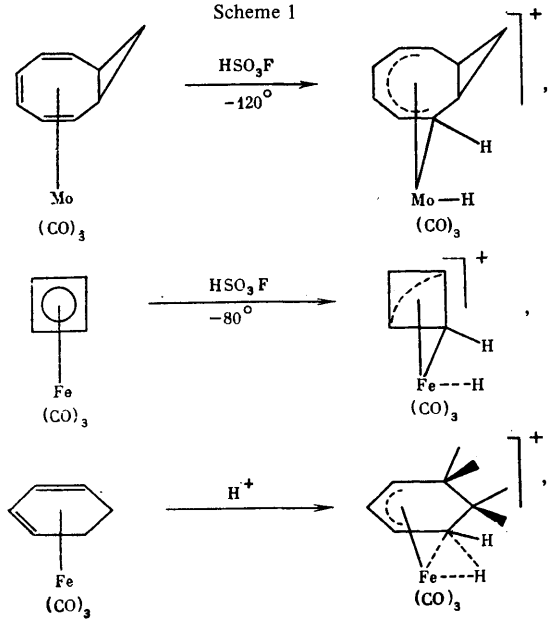
bond is not formed despite the presence of the electron-deficient centre. There exists a single brief review devoted to three-centre M...H−C bonds,[13] whose authors proposed a new term for such bonds and hydrogen atoms—"agostic" C−H bonds or hydrogen atoms. This term is frequently used in the foreign literature.

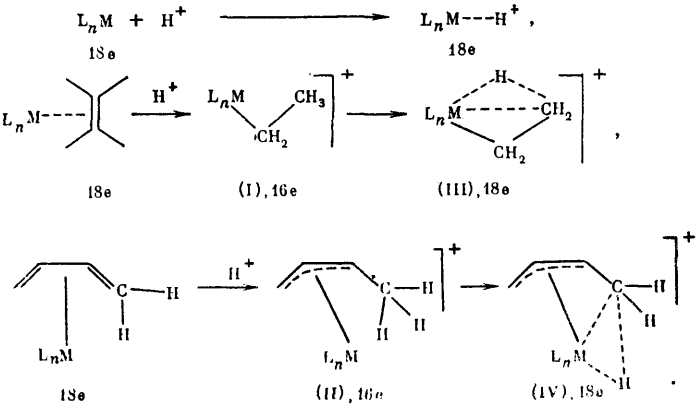
II. EARLY STUDIES

The first information about the possibility of the coordination of C−H bonds to transition metals appeared in 1968−1975. In many cases, the signals of the CH_2 and CH_3 protons in the H NMR spectra of the complexes were observed in the high field region (δ ranging from 0 to −12 p.p.m. and above), which is known to be characteristic of metal hydrides (see the review of Kaesz and Saillant[1]). It was shown on the basis of XRD data that in many cases there is a weak interaction in ruthenium, palladium, and platinum complexes between the metal and the hydrogen in the *ortho*-position in the arylphosphine ligands. On the other hand, owing to the insufficient accuracy of the XRD method, the positions of the hydrogen atoms could not be as a rule located by direct procedures. The conclusion that there is an interaction between the C−H bond and the metal was reached on the basis of the presence of short intramolecular M...H contacts, significantly shorter than the sums of the van der Waals radii of M and H. Interactions of this type have been described for the following complexes: $Ru(PPh_3)_3Cl_2$ (Ru...H distance 2.59 Å);[14] *trans*-$Pd(PPhMe_2)_2I_2$ (Pd...H 2.8 Å);[15] $Rh(PPh_3)_3^+ClO_4^-$ (Rh...H 2.56 Å);[16] $Pd(PPh_3)_2(Br)(CR{=}CR.CR{=}CHR)$, where R = COOMe (Pd...H 2.3 Å);[17] $Ni[Et_2B.(pyrazolyl)_2]_2$;[18] $Mo[Et_2B(pyrazolyl)_2](\eta^3\text{-}CH_2CHPhCH_2)(CO)_2$ [Mo...H 2.27 Å, δ(Mo−H) = 2.4 p.p.m.].[19]

More than 10 years ago, a series of studies were published[20-24] in which π,σ structures with protonation of the metal and the simultaneous formation of M−C σ-bonds were proposed for the protonated forms of the η-complexes solely on the basis of ^1H and ^{13}C NMR data (Scheme 1). Later these results were revised and it was concluded that an M−C σ-bond does not arise in such cases. The formation of the Fe...H−C 2e, 3c-bond was first postulated for the protonated form of the complex $(\eta^4\text{-}C_6H_8)Fe(CO)_3$.[25]

Scheme 1





During the last 8−10 years extensive experimental data have accumulated on the synthesis and properties of CHB both in the crystal (structural methods) and in solutions, a systematic account of which is given below.

III. METHODS OF FORMATION

An exceptionally wide variety of structures are characteristic of the complexes of the type considered. Their general property is that the metal atom is an electron-deficient centre. In the presence of electron-donating ligands or solvents (L), electron-deficient complexes are usually stabilised as a result of the addition of L to an unoccupied coordination site. However, if the system has no electron-donating ligands, then one of the possible ways in which the electron deficiency can be partially or completely made good and a stable 18-electron shell created involves the intramolecular coordination of an unoccupied orbital of the metal (LUMO) to one of the electron pairs of a C−H bond with formation of an M...H−C 2e, 3c-bond. In this case the C−H bond plays the role of a kind of two-electron "ligand". Depending on the geometry of the M...H−C fragment, such bonds can be divided by convention into "open" (M−H−C angle 120−130° and above), and "closed" (with an angle of 70−90°). There is no clear-cut boundary between these types.

Evidently, the formation of CHB is to be expected primarily among electron-deficient complexes of the elements at the beginning of the Periods (Sc, Ti, V, and their analogues), for which a large number of deviations from the 18-electron rule are known. Indeed, among the 12−16-electron complexes of Y, Ti, Zr, and Ta, numerous examples of the formation of M...H−C bridge bonds have been found. The formation of these bonds proved to be characteristic of a large group of 14- and 16-electron alkylidene complexes of Ta (and also Nb and W), typical representatives of which are the structurally characterised complexes $Ta(=CH-CMe_3)(\eta\text{-}C_5Me_5).(C_2H_4)(PMe_3)$, $[Ta(=CH-CMe_3)(PMe_3)Cl_3]_2$, and $W(=CH-CMe_3)(CO)(PMe_3)_2Cl_2$. Since the identification of the M...H−C bridge bonds in the crystal is based exclusively on structural research methods and in solutions mainly on NMR data, the properties and characteristics of the bridge bonds in the solid phase and in solutions will be examined in greater detail below in Sections IV and V.

Several reactions in which there is a possibility of the formation of CHB are known for compounds of the elements in the middle of the Period (Group VI−VIII) elements. The protonation and decarbonylation reactions have been studied in greatest detail.

Table 1. The formation of complexes with a bridging hydrogen atom on protonation or intramolecular isomerisation.

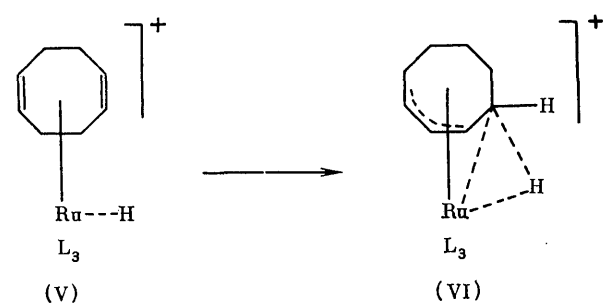
Precursor	Protonated form with bridging hydrogen atom	Acid	Refs.
$Mo_2(\eta\text{-}C_6Me_6)(\eta\text{-}Cp)_2$	$[Mo_2(\eta\text{-}C_6Me_6\text{-}\mu\text{-}H)(\eta\text{-}Cp)_2]^+$	$HBF_4\cdot Et_2O$, CF_3SO_3H	[29, 30]
$Mo(\eta^5\text{-}C_9H_7)(\eta\text{-}C_{13}H_{13})$	$[Mo(\eta^5\text{-}C_9H_7)(\eta\text{-}C_{13}H_{13}\text{-}\mu\text{-}H)]^+$	CF_3SO_3H	[31]
$Mo(\eta^4\text{-}C_4H_6)_2(PMe_3)_2$	$[Mo(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_4H_6\text{-}\mu\text{-}H)(PMe_3)_2]^+$	HBF_4/MeOH	[32]
$ReW(\mu\text{-}CHC_6H_4Me)(\mu\text{-Dppm})(CO)_7$ *	$[ReW(\mu\text{-}CH_2C_6H_4Me)(\mu\text{-Dppm})(CO)_7]^+$	$HBF_4\cdot Et_2O$	[33]
$[Mn(\eta^4\text{-}C_6H_8)(CO)_3]^-$	$Mn(\eta^5\text{-}C_6H_8\text{-}\mu\text{-}H)(CO)_3$	H_2O	[34]
$[Mn(\eta^4\text{-}C_6H_7R)(CO)_3]^-$	$Mn(\eta^5\text{-}C_6H_7R\text{-}\mu\text{-}H)(CO)_3$	H_2O	[35—38]
$Fe_2(\eta\text{-}Cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$	$[Fe_2(\eta\text{-}Cp)_2(CO)_2(\mu\text{-}CO)(\mu CH_2\text{-}\mu\text{-}H)]^+$	CF_3SO_3H, HBF_4	[39]
$Fe(\eta^4\text{-Dien})(P(OMe)_3)_3$	$[Fe(\eta^3\text{-Enyl-}\mu\text{-}H)(P(OMe)_3)_3]^+$		[40, 41]
Dien = cyclo-octa-1,3-diene	Enyl = cyclo-octenyl	HBF_4/MeOH, CF_3COOH/MeOH	[40, 41]
Butadiene	butenyl	»	[40, 41]
2-Methylbutadiene	2-methylbutenyl	»	[40, 41]
2,3-Dimethylbutadiene	2,3-dimethylbutenyl	»	[40, 41]
Cyclohexa-1,3-diene	cyclohex-1-en-3-yl	»	[40, 41]
Cycloheptа-1,3-diene	cyclohept-1-en-3-yl	»	[40, 41]
$Fe_2(\eta\text{-}Cp)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-Dppm})$	$[Fe_2(\eta\text{-}Cp)_2(\mu\text{-}CO)(\mu\text{-}CH_2\text{-}\mu\text{-}H)(\mu\text{-Dppm})]^+$	HPF_6	[42]
$[HFe_5C(CO)_{14}]^-$	$HFe_4(C\text{-}\mu\text{-}H)(CO)_{13}$	HCl	[43]
$[Ru(\eta^4\text{-}C_8H_{12})(H)(L)_3]^+$	$[Ru(\eta^3\text{-}C_8H_{12}\text{-}\mu\text{-}H)(L)_3]^+$	—	[44]
L=$P(OMe)_2Ph$, $P(OMe)Ph_2$, PMe_3 $PMePh_2$; L$_3$=$MeC(CH_2PPh_2)_3$			
$Ru(\eta^6\text{-}Me_6C_6)(\eta^4\text{-}C_{10}H_{12})$	$[Ru(\eta^6\text{-}Me_6C_6)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	HPF_6	[45]
$Ru(\eta^6\text{-}Me_6C_6)(\eta^4\text{-}C_8H_8)$	$[Ru(\eta^6\text{-}Me_6C_6)(\eta^3\text{-}C_8H_8\text{-}\mu\text{-}H)]^+$	HBF_4, HBF_6	[46]
$Ru(L_2)(L')(\eta\text{-}Me_4C_6(=CH_2)_2)$	$[Ru(L_2)(L')(\eta\text{-}Me_4C_6(CH_2)(CH_2\text{-}\mu\text{-}H)]^+$	HPF_6	[47]
L_2=$Ph_2PCH_2CH_2PPh_2$, L'=PMe_2Ph			
$Ru_3(\mu\text{-}H)_3(\mu\text{-}CEt)(CO)_9$	$[Ru(\mu\text{-}H)_3(\mu\text{-}EtC\text{-}\mu\text{-}H)(CO)_9]^+$	CF_3SO_3H	[48]
$Os(\eta^6\text{-}Me_3C_6H_3)(\eta^4\text{-}C_{10}H_{12})$	$[Os(\eta^6\text{-}Me_3C_6H_3)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CF_3SO_3H, FSO_3H	[45]
$Os_3(\mu\text{-}H)_3(\mu\text{-}MeC)(CO)_9$	$[Os(\mu\text{-}H)_3(\mu\text{-}MeC\text{-}\mu\text{-}H)(CO)_9]^+$	CF_3SO_3H	[48]
$Co(\eta^5\text{-}C_5Me_4R)(\eta^3\text{-}C_2H_4)_2$, R=Me, Et:	$[Co(\eta^5\text{-}C_5Me_4R)(\eta^3\text{-}C_2H_4)(\sigma\text{-}C_2H_4\text{-}\mu\text{-}H)]^+$	HBF_4	[49]
$Co(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)P(C_6H_4Me)_3$	$[Co(\eta^5\text{-}C_5Me_5)(\sigma\text{-}C_2H_4\text{-}\mu\text{-}H)P(C_6H_4Me)_3]^+$	HBF_4	[50, 52]
$Co(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_2H_3R)P(OMe)_3$, R=Me, Et	$[Co(\eta^5\text{-}C_5Me_5)(\sigma\text{-}C_2H_3R\text{-}\mu\text{-}H)P(OMe)_3]^+$	HBF_4	[51]
$Rn(\eta^5\text{-}C_5R_5)(\eta^4\text{-}C_{10}H_{12})$, R=H, Me;	$[Rh(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	HPF_6	[45]
$Rh(\eta^4\text{-}C_7H_8)(\eta^5\text{-}Me_2C_2B_9H_9)^-$	$Rh(\eta^3\text{-}C_7H_8\text{-}\mu\text{-}H)(\eta^5\text{-}Me_2C_2B_9H_9)$	CF_3COOH	[53]
$Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4H_6)$	$[Rh(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_4H_6\text{-}\mu\text{-}H)]^+$	HBF_4	[54]
$Ir(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_{10}H_{12})$	$[Ir(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	HPF_6	[45]

*Dppm = $Ph_2PCH_2PPh_2$.

1. Protonation

It is well known that the η-complexes and low-valence carbonyl complexes of transition metals constitute a new class of bases—polyfunctional organometallic Lewis bases. They interact readily with various electrophiles (E)—including protic and aprotic acids, the attack by E being as a rule directed to the centre with the highest basicity. In complexes of the type L_nM, there is a possibility of the addition of E both to the metal atom and to the ligands (L). The relative basicities of the different centres and the direction of attack by E depend on the structure of the complex, the nature of the metal, the character and type of the ligand environment, and the nature of E (see the relevant reviews[26-28]). If the 18-electron complex L_nM is protonated at the metal atom, then the product is the cation $[L_nM-H]^+$, where the metal retains the 18-electron environment and there are no grounds to expect the formation of a CHB. However, if the proton adds to the carbon atom of the C=C bond in the coordinated olefin or diene ligand, then the number of electrons supplied by the ligand for binding to the metal diminishes by one. η^2-Olefins or η^4-dienes (donors of two or four electrons) are then converted respectively into η^1-alkyl or η^3-allyl ligands (donors of one and three electrons). Taking into account the positive charge, the formal electronic environment of the metal in the monocationic complexes (I) and (II) arising on protonation can be stabilised as a result of the coordination of the unoccupied orbital of the metal to the electrons of a suitably directed C—H bond with conversion into cationic or neutral (if an anionic complex has been protonated) CHB (III) and (IV). The instances of the formation of CHB on protonation of 18-electron precursors are compiled systematically in Table 1.

The intramolecular isomerisation of hydride complexes, known in relation to the cationic dieneruthenium hydride complexes,[44] bears a close analogy to protonation by acids (HBF_4, HPF_6, CF_3SO_2OH, etc.). The isomerisation of the dienemetal hydride complexes to CHB can be regarded as "intramolecular protonation":



(V) (VI)

The cationic η^4-dieneruthenium hydride complexes (V) have been isolated and characterised; they are stable in solution at temperatures below −10 °C, while in the temperature range 0—60 °C (depending on the size of L and the type of the donor atom), compounds (V) isomerise spontaneously and irreversibly to the η^3-allyl complexes (VI) with a bridging hydrogen atom as a result of the intramolecular proton transfer from the metal to the cyclo-octadiene ligand.[44] From this it follows that in the given case the η^3-allyl

CHB of type (VI) are thermodynamically more favourable than their η^4-dienemetal hydride precursors. The rate of isomerisation (V) → (VI) depends on the size of L and decreases in the following sequence of groups L: $P(OCH_2CMe_3)_3$ > $P(OMe)Ph_2$ ≃ PMe. .Ph_2 > PMe_2Ph > $MeC(CH_2PPh_2)_3$ > $P(OMe)_2Ph$ > PMe_3 ≃ $AsMePh_2$. When L = $P(OMe)_3$, $AsMe_3$, or $AsMe_2Ph$, there is no isomerisation.[44]

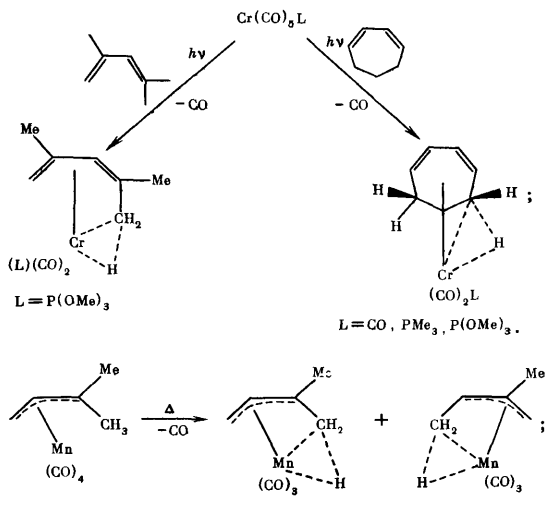
An important feature is that in the reactions involving the protonation of the η-complexes by strong acids, unstable olefin- or diene-metal hydride intermediates are formed initially as a result of the kinetically controlled rapid attack by H^+ on the metal atom. As a consequence of the subsequent migration of hydrogen from the metal to a carbon of the olefin or diene ligand, the intermediates are converted into thermodynamically more favourable cationic CHB. The dieneruthenium hydride complexes having the general formula $[(\eta^4\text{-}C_8H_{12})RuL_3H]^+$ proved to be sufficiently stable to be isolated and and characterised, but in the case of other metals they can be kinetically or thermodynamically unstable. In the reaction of the cationic dihydride complex $[Ir(H)_2(PPh_3)_2(Me_3CO)_2]^+$ with 2,3-dimethylbutadiene, the η^3-allyl CHB $[Ir(H)(PPh_3)_2(\eta^3\text{-}CH_2CMeCMe}.$.$CH_2\text{-}\mu\text{-}H)]^+$ (VII) was isolated as the final product. Apparently initially two acetone molecules are substituted by the diene ligand with formation of the thermodynamically unstable dieneiridium hydride complex $[IrH_2(PPh_3)_2(\eta^4\text{-}CH_2 = CMeCMe = CH_2)]^+$, which then affords compound (VII) as a result of the rapid intramolecular proton transfer from iridium to the diene.[55]

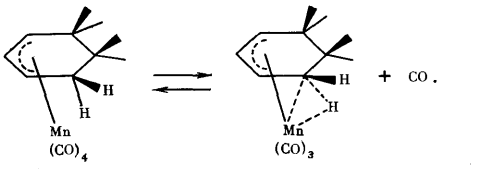
Protonation by strong acids is most characteristic of complexes of metals in the middle of the Periods (Mo, Mn, Fe, Co). Such reactions are unknown for the elements at the beginning and end of the Periods.

2. Decarbonylation

The second type of processes leading to the formation of CHB involves photochemical or thermal decarbonylation of the carbonyl complexes. On irradiation with UV light or on heating, the abstraction of one or several CO groups results in the formation of electron- and coordination-unsaturated intermediates, which can afford CHB in the presence of diene ligands, as shown in Scheme 2 for manganese and chromium complexes.

Scheme 2



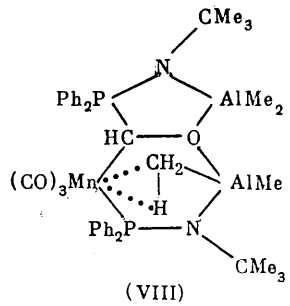


UV irradiation of $Cr(CO)_5L$ [L = P(OMe)] in pentane at 293 K in the presence of 2,4-dimethylpenta-1,3-diene did not yield the expected complex $Cr(CO)_3(L)(\eta^4\text{-}C_7H_{12})$, as in the reactions with other dienes.[56] Instead, the elimination of three CO groups and coordination of the $Cr(CO)_2(L)$ fragment to the diene led to the isolation of a CHB having the structure $Cr(CO)_2(L)(\eta^4\text{-}C_7H_{11}\text{-}\mu\text{-}H)$, in which the diene ligand is linked to chromium via two C=C bonds and the bridging hydrogen atom.[57] The photochemical decarbonylation of $Cr(CO)_5L$, where L = CO, PMe_3, or $P(OMe)_3$, in the presence of cyclohepta-1,3-diene, affording the complexes $Cr(CO)_2(L)(\eta^4\text{-}C_7H_9\text{-}\mu\text{-}H)$, proceeds analogously.[58] In both cases, the CHB isolated were characterised structurally. Thermolysis of the η^3-allyl complex $Mn(CO)_4(\eta^3\text{-}CH_2CHCMe_2)$ in toluene at 110 °C leads to the abstraction of CO with formation of a mixture of isomeric complexes with a bridging hydrogen atom: $Mn(CO)_3$. .$(\eta^3\text{-}CH_2CHCMe\text{-}CH_2\text{-}\mu\text{-}H)$.[59] The thermal decarbonylation of the enyl complex Mn(η^3-cyclohexenyl)$(CO)_3L$, where L = phosphine or phosphite, proceeds analogously[59] (Scheme 2).

3. Ligand Substitution

A number of instances of the formation of CHB as a result of ligand substitution are known. One of them involves the displacement of two acetone molecules by 2,3-dimethylbutadiene in an iridium complex, which was already mentioned above. The interaction of salts of the square-planar cation $[Ir(PPh_3)_2(\eta^4\text{-}C_8H_{12})]^+A^-$ (A = PF_6, BF_4, or SbF_6) with gaseous H_2 in the presence of 8-methylquinoline (in CH_2Cl_2 at 0 °C) yielded, as a result of the oxidative addition of H_2 with simultaneous displacement of cyclooctadiene, cationic iridium(III) complexes having the composition $[IrH_2(PPh_3)(\mu\text{-}H\text{-}CH_2C_9H_6N)]^+A^-$ in which 8-methylquinoline is linked to iridium via a nitrogen atom and one bridging H atom in the methyl group.[60]

The substitution of one of the ligands L = PMe_3 and the abstraction of NaCl in the interaction Of $Mo(CO)(CO)(\eta^2\text{-}C,O\text{-}C(O)CH_2SiMe_3)L_3$ with sodium dimethyldithiocarbamate results in the formation of the complex $Mo(CO)(S_2CNMe_2)(L)_2\text{-}C(O)CH_2\text{-}\mu\text{-}H$, where the acetyl group is linked to Mo via a Mo–C σ-bond and a bridging H atom.[61] The above cationic dieneruthenium hydride complexes $[Ru(H)(L)_3(\eta^4\text{-}1,5\text{-}C_8H_{12})]^+$ or the products of their intramolecular isomerisation, namely CHB with the cyclooctenyl fragment $[Ru(\eta^3\text{-}C_8H_{12}\text{-}\mu\text{-}H)L_3]^+$ are converted into the corresponding cationic CHB of the type $[Ru(L)_3(\eta^3\text{-Enyl-}\mu\text{-}H)]^+$, where L = PMe_2Ph, PMe_3, $P(OMe)_2Ph$, or $P(OMe)Ph_2$, in reactions with 1,3-dienes (cyclohepta-1,3-diene, cyclohexa-1,3-diene, butadiene) as a result of the displacement of cyclo-octa-1,3-diene.[62] CHB formed in the following reactions have been obtained and characterised structurally: cocondensation of chromium vapour with cyclo-octa-1,3-diene or cyclo-octa-1,5-diene in the presence of PF_3 leading to the formation of the complex $Cr(\eta^5\text{-}C_8H_{10}\text{-}\mu\text{-}H)(PF_3)_3$;[63] the reaction of $Mn(CO)_5H$ with two moles of the ligand $Ph_3PN(CMe_3)$. .$AlMe_2$ leading to the formation of the bicyclic complex (VIII):[64,65]



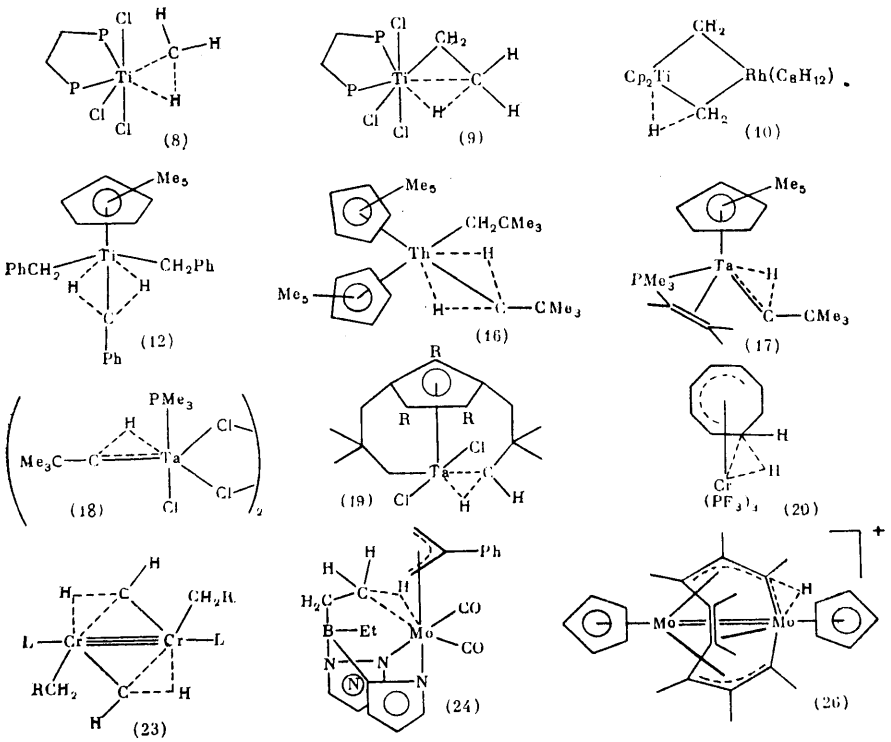
(VIII)

It has been suggested that the 17-electron radical-cations, formed in the one-electron electrochemical oxidation of the 18-electron complexes $(\eta\text{-Cp})_2W(R)(R')$, where R and R′ are an alkyl or an aryl group, can be stabilised via the formation of three-centre three-electron W...H−C bonds with the α- or β-hydrogen atom of the residue R.[66] The formation of cationic or neutral CHB in the protonation reactions is summarised in Table 1. The converse reaction is also known, namely the deprotonation of a neutral cluster with formation of an anionic CHB. It has been shown that the neutral tetrahedral cluster $Fe_3(CO)_9(\mu\text{-H})_3(\mu^3\text{-HC})$, not containing agostic H atoms, exists in solution in equilibrium with a further two isomeric clusters $Fe_3(CO)_9(\mu\text{-H})_2(\mu^3\text{-HC-}\mu\text{-}\textit{H})$ [isomer (A)] and $Fe_3(CO)_9(\mu\text{-H})(\mu^3\text{-HC-}\mu\text{-}\textit{H}_2)$ [isomer (B); the agostic hydrogen atoms are distinguished by being italicised]. In the isomers (A) and (B), there are respectively one and two Fe...H−C 2e, 3c-bonds. Deprotonation of $Fe_3(CO)_9(\mu^3\text{-HC})$ by treatment with an excess of $(PPh_3)_2N^+Cl^-$ leads to the formation of the anionic CHB $Fe_3(CO)_9$. $.(\mu\text{-H})(\mu^3\text{-HC-}\mu\text{-H})^-$.[67]

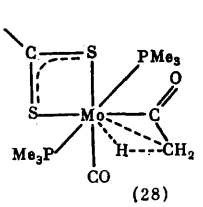
IV. THE STRUCTURE IN THE CRYSTAL ACCORDING TO DATA OBTAINED BY STRUCTURAL METHODS

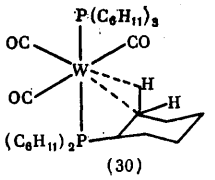
The identification of the M...H−C bridge 2e, 3c-bonds in the crystal is based exclusively on data obtained by structural research methods—X-ray diffraction analysis and neutron diffraction (ND). Scheme 3 presents formulae for a series of structurally characterised CHB and Table 2 summarises certain crystal-chemical data for the M...H−C bridged fragments: the M...H, C−H, and M−C distances and the M−H−C angle. It was not until 1979−1981 that it became possible to understand the fine features of the structure of the CHB as a whole class of complexes with a new type of coordination of the hydrogen atom in a C−H bond to the metal in connection with the considerable improvement of the accuracy of the XRD method and the publication of a series of pioneering studies in which the structures of CHB containing tantalum,[84,85] manganese,[35,95] and iron[100,101] were established.

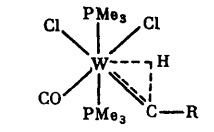
Scheme 3

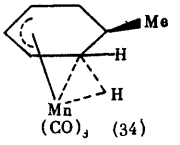


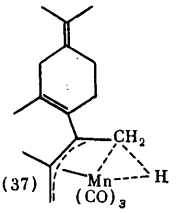
the numbering of the compounds is the same as in Table 1

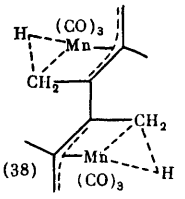

(28)

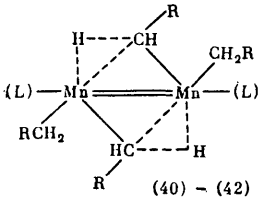

(30)

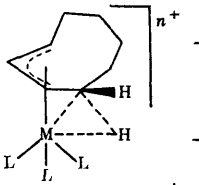

(32) R = CMe_3; (33) R = Ph


(34)

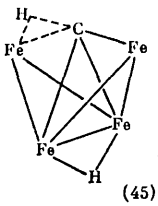

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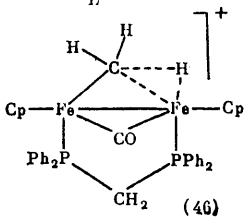

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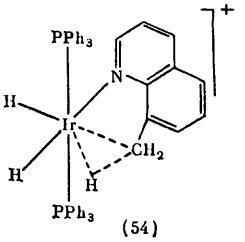

(40) – (42)



M	L	n	№
Fe	$P(OMe)_3$	1	(43)
Fe	$P(OMe)_3$	0	(44)
Ru	$P(OMe)Ph_2$	1	(47)


(45)


(46)


(54)

It is possible to differentiate the following characteristic features of the bridged M...H–C fragments. The M...H distances involving the bridging hydrogen atoms in the CH_n fragment (n = 2,3) are greater on average by 10–20% compared with the usual ranges of M–H bond lengths for terminal hydrido-ligands (according to data in the review of Teller and Bau[7]). The C–H distances determined from XRD data are known to be always too low by 0.1–0.15 Å by virtue of the characteristics of the method itself. One can therefore compare only the C–H distances obtained by the ND method, from which it follows that the C–H bonds coordinated to the metal are extended (loosened). According to ND data, the C–H distances in CHB are 1.10–1.19 Å, which is approximately 5–10% greater than the average C–H distances involving sp^3-carbon atoms (1.08 to 0.19 Å).

The M...H distances obtained by the ND method are compared in Table 3 with the sum of the covalent radii of the M atoms (according to the data of Andrianov et al.[118] and Churchill[119]) and H atoms (0.37 Å) and the C–H bond lengths derived from ND data are also listed. Except for complexes of Group IV metals (Ti, Th), the M...H distances exceed by less than 10% the sum of the covalent radii of M and H. On this basis, one can apparently conclude that, at least in the cases quoted, the M...H bridge bonds, although extended, do not differ very greatly from the terminal M–H bonds in metal hydride complexes.

A method has been proposed[60] for the estimation of the strength of the interaction of the C–H bond with the metal and of the strength of the bond produced. The distance d_A between the metal atom and the point A, where according to the author's hypothesis the centre of the electron pair of the C–H bond is located and through which coordination to the unoccupied metal orbital takes place, is calculated from the experimental distances d(MH), d(MC), and the dimensionless constant a = 0.28 (the ratio of the covalent radius of the hydrogen atom to the length of the "usual" C–H sp^3-bond).

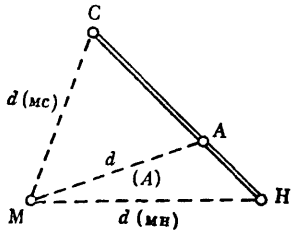


Table 2. Structural data for complexes with a bridging hydrogen atom.

No.	Compound	Method	Distance, Å			M...H–C angle, deg	r_A (Ref.60)	Refs.
			M···H	M–C	C–H			
1	Y (C_5Me_5)$_2$N($SiMe_3$)($SiMe_2CH_2$-μ-H)	XRD	2.45; 3.00	2,970	1.00; 1.06	110.4; 101.6	—	[68]
2	Y (C_5Me_5)$_2$C-μ-H ($SiMe_3$) ($SiMe_2CH$-μ-H_2)	XRD	2 53 (C-μ-H)	2,468	—	84	—	[68]
			2.45; 3.00 (SiCH-μ-H)	2,878	—	—	—	[68]
3	Nd (η^5, η^5-$C_5Me_4SiMe_2C_5Me_4$) C-μ-H ($SiMe_3$)$_2$	XRD	—	2,862	—	—	—	[69]
4	Sm (C_5Me_5)$_2$ (*o*, μ-HC_5H_4N=NC_5N-*o*, μ-H) Sm (C_5Me_5)$_2$	XRD	2.29	—	—	—	—	[70]
5	Yb (C_5Me_5)$_2$ [(μ-H-)$_2$C=CH_2] Pt (PPh_3)$_2$	XRD	2.58; 2.64	2.770; 2.793	—	—	—	[71]
6	Yb (Dmpe) [N ($SiMe_3$)$_2$]$_2$	XRD	2.77; 2.86	3,04	—	—	—	[72]
7	Cl_2 (CH_3) Ti (μ-Cl)$_2$ Ti (CH_2-μ-H) Cl_2	XRD	1.92	2,068	1.19	78	—	[73]
8	Ti (CH_2-μ-H) (Dmpe) Cl_3	XRD	2.03	2.149	1.00	80	0.69	[74]
		ND	2,447	2.122	1.095	93.5		[75]
9	Ti (CH_2CH_2-μ-H) (Dmpe) Cl_3	XRD	2.22	2.524	1.04	88	0.98	[75, 76]
10	Ti (Cp)$_2$ (CH_2-μ-H) (μ-CH_2) Rh (C_8H_{12})	XRD	2.024	2.294	0.98	61	—	[77]
11	$TiMe_{1,3}Cl_{0,7}$ (Dmpe)$_2$	XRD	—	2.351	—	—	—	[78]
12	Ti (η-C_5Me_5) (CH_2Ph)$_3$	XRD	2.32; 2.37	2.081	—	—	—	79]
13	Zr (Cp)$_2$ (Cl) (μ-MeCH) Zr (Cl) (C_5H_4Me)$_2$	XRD	2.211	2.585	1.018	99.7	—	[80]
14	Zr (Dmpe) (CH_2SiMe_3)$_4$	XRD	2.48	2,215	—	—	—	[81]
15	[Hf (η-C_5Me_4) Cl—μ-(CHCH$_2$CMe=CMeCH$_2$)$_2$	XRD	2.21	2.134	—	—	—	[82]
16	Th (η-C_5Me_5)$_2$ (CH_2CMe_3)$_2$	ND	2.597; 2.648	2.456	1.114; 1.122	—	—	[83]
17	Ta (η-C_5Me_5) ($CHCMe_3$) (η-C_2H_4) (PMe_3)	ND	2.042	1.946	1.135	—	0.61	[84. 85]
18	[Ta ($CHCMe_3$) (PMe_3) Cl_3]$_2$	ND	2.119	1.898	1,131	—	0.68	[84. 85]
19	Ta (η-C_5R_5) ($CH_2CMe_2CH_2$)$_2$ Cl_2	XRD	2.30	2.176	1.102	—	—	[86]
20	Cr (η-C_6H_{10}-μ-H) (PF_3)$_3$	XRD	1.8	2,352	—	—	—	[63]
21	Cr (η^4-C_7H_{11}-μ-H) (CO)$_2$ P (OMe_3)	XRD	1.94	2.399	—	101.1	—	[57]
22	Cr(η^4-1,3-cyclo-C_7H_9-μ-H)(CO)$_2$$PMe_3$	XRD	1.85	2.355	1.16	100.4	—	[58]
23	Cr_2 (CH_2SiMe_3)$_4$ (PMe_3)$_2$	XRD	2.236; 2.262	2.266 cp	0.910; 1.018	—	—	[87]
24	Mo [B (Pir)$_2^*$ (Et) (CH_2CH_2-μ-H)] (CO)$_2$ (η^3-C_3H_4Ph)	XRD	2.27	3.055	0.97	136	1.12	[19]
25	Mo ($Ph_2PCH_2CH_2PPh_2$)$_2$ (CO)	XRD	2.98	—	—	—	—	[88]
26	[Mo_2 (η-C_8Me_8-μ-H) (Cp)$_2$]$^+$	XRD	1.88	2.196	0.89	99	0.61	[29, 30]
27	[Mo (η-C_9H_7) (η, σ-$C_{12}H_{13}$-μ-H)]$^+$	XRD	1.80	2.391	1.08	110	—	[31]
28	Mo ($COCH_2$-μ-H) (S_2CNMe_2) (CO) (PMe_3)$_2$	XRD	2.06	2.60	1.00	111	0.84	[61]
29	WRe (μ-H-CHC_6H_4Me) ($Me_2PCH_2PMe_2$)(CO)$_7$	XRD	2.08	2,541	0.86	113	—	[33]
30	W [P (C_6H_{11})$_3$]$_2$ (CO)$_3$	XRD	2.27	2.945	0.95	127	—	[89 90]
31	W[P(iso-C_3H_7)$_3$]$_2$(CO)$_3$	XRD	—	3,027	—	—	—	[89]
32	W ($CHCMe_3$) (CO) (PMe_3)$_3$$Cl_2$	XRD	1.835	1,859	1.053	75	—	[91. 92]
33	W (CHPh) (CO) (PMe_3)$_2$$Cl_2$	XRD	—	1.860	—	—	—	[93, 94]
34	Mn (η^3-MeC_6H_8-μ-H) (CO)$_3$	XRD	1.86	2.301	1.07	100	0.75	[35]
		ND	1.84	2.34	1.19	99		[95]
35	Mn (CO)$_3$ (μ-σ:η^3-$CH_2CMeCHMe$) (μ-PPh_2) (μ-CO) MoCp	XRD	2.02	2.346	—	—	—	[96]
36	Mn (CO)$_3$ (μ-σ:η^4-$CHCHCH_2CHPPh_2$) Mo (CO) Cp	XRD	2.29	2.245	—	—	—	[96]
37	Mn (CO)$_3$ ($C_{15}H_{23}$)	XRD	2.296; 2.298	1.901; 1,880	—	98.1; 101.3	—	[97]
38	Mn_2 (CO)$_8$ ($C_{10}H_{16}$)	XRD	2 291	1.816	—	100,7	—	[97]
39	Mn (CO)$_3$$CHOAlMe_2N$ (CMe_3) Al (μ-H-CH_2) (Me)	XRD	1.91	2.45	0.80	124	—	[64, 65]
40	Mn_2 (CH_2Ph)$_4$ (PMe_3)$_2$	XRD	2.20	2.391	—	—	—	[99]
41	Mn_2 (CH_2SiMe_3)$_4$ (PMe_3)$_2$	XRD	2.29	2.369	—	—	—	[98, 99]
42	Mn_2 (CH_2SiMe_3)$_4$ ($PMePh_2$)$_2$	XRD	2.15	2.389	—	—	—	[99]
43	[Fe (η^3-C_8H_{12}-μ-H) (P (OMe_3)$_3$]$^+$	XRD	1.95	2.384	1.07	100	0,79	[100, 101]
		ND	1,874	2.362	1.164	99.4		[101]
44	Fe (η^3-C_8H_{12}-μ-H) (P (OMe_3)$_3$	XRD	2.77	2,983	0.99	93	—	[102]
45	Fe_4 (μ-CH) (H) $(CO)_{12}$	XRD	1.80	1,926	1,00	82	0.59	[103]
		ND	1,755; 1.747	1.927; 1 920	1 191; 1,176	84; 84	—	[104]
46	[Fe_2 (μ-CH_2-μ-H) (μ-CO) ($Ph_2PCH_2PPh_2$) (Cp)$_2$]$^+$	XRD	1.64; 1.78	2.108; 2.118	1 06; 0.83	101; 103	0.65	[42]
47	[Ru (η^3-C_8H_{12}-μ-H) (P (OMe) Ph_2)$_3$]$^+$	XRD	2.08	2 592	1.14	103	—	[105]
48	[Ru (η^3-C_4H_6-μ-H) (PMe_2Ph)$_3$]$^+$	XRD	1.84	2.38	—	—	—	[62]
49	RuCl ($C_{21}H_{34}$-μ-H)	XRD	2,10	—	1.04	118	—	[106]
50	[Os (η-$Me_3C_6H_3$) (η-$C_{10}H_{12}$-μ-H)]$^+$	XRD	1.81	2,30	0,95	110	—	[45]
51	[Co (η-C_5Me_5) (CH_2CH_2-μ-H) P (C_6H_4Me-*n*)$_3$]$^+$	XRD	1.46	2.128	1,31	—	—	[50]
52	Co (η^3-C_8H_9-μ-H) (C_6H_{11})$_2$$PCH_2CH_2P$ (C_6H_{11})$_2$	XRD	1.85	2.297	—	—	—	[107]
53	Rh (η-C_7H_8-μ-H) (η^5-1,2-$Me_2C_2B_9H_9$)	XRD	1.9	2.36	—	108	—	[53]
54	[IrH_2 (PPh_3)$_2$(N, C-8-CH_2—μ-H-C_9H_6N)]$^+$	XRD	2.08	2.69	0,96	119	0.91	[60]
55	Pd (N (NMePh)=CMe_2)$_2$$Cl_2$	XRD	2.36	—	—	—	—	[108]
56	Pd(1-methylcytosine)$_2$$Cl_2$	XRD	2.66	3,128 (Pd—N)	0 82 (N—H)	118	—	[109]
57	Pd (NMe=CHPh)$_2$$Cl_2$	XRD	2.44	3,22	1.01	131	1.30	[110]
58	Pd [(η^5-NC_4H_4)Mn (CO)$_2$$PPh_2C_6H_4$-μ-H]$_2$$Cl_2$	XRD	2.68	—	0.88	154	—	[111]
59	Pd (PPh_3)$_2$ (CR=CR—CR=CR-μ-H) Br, R = COOMe	XRD	2.30	3.19 [60]	—	137	1.26	[17]
60	[Pd (PPh_2CMe_3)$_2$]$_3$	XRD	2.70	3.45	1.05	128	1.56	[112]
61	[Pt (PPh_2CMe_3)$_2$]$_2$	XRD	2.77	3.46	0.97	126	1.60	[112]
62	*trans*- $PtCl_2$ [MeC_6H_3NN=C (μ-H) $C_6H_2Me_3$] ($AsEt_3$)	XRD	2.43	—	1.02	117	—	[113]
63	*cis*-Pt (*o*-$Ph_2PC_6H_4NC$ (O)C_6H_4) (*o*-$Ph_2PC_6H_4NHC$ (O) Ph)	XRD	2.318	3,24 (N—Pt)	1.04 (N—H)	—	—	[114]
64	[$PtCl_4$-*cis*-$PtCl_2(NH_2Me)_2$]$^{2-}$	ND	2.262	—	1.032(N—H)	167.1	—	[115]
65	Cu (C_7H_9-μ-H) ($H_2NCH_2CH_2NHCH_2CH_2NH_2$)	XRD	2.01	2.78	—	158	—	[116]
66	Au (PPh_3)C_5H_4C (=O) C_5H_4-μ-H	XRD	2,94	—	0.98	—	—	[117]

*Pir = pyrazolyl.

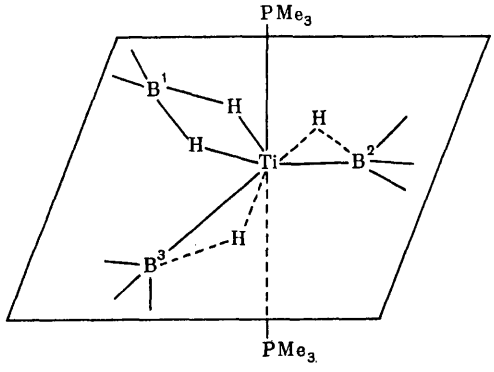
In order to be able to compare the complexes of different metals, the difference $r_A = d_A - r_M$, where r_M is the covalent radius of the metal, was adopted as a criterion of the estimate. It has been suggested that r_A be treated as a kind of "covalent radius" of the bonding electron pair. The greater the value of r_A, the weaker the M...H–C interaction. The values of r_A are listed in Table 2. One can differentiate arbitrarily three groups of compounds. Within the framework of the given approach, the bridge bonds are the strongest for Fe_4(μ-CH)(H)$(CO)_{12}$, [Mo_2(η-C_8Me_8-μ-H)(Cp)$_2$]$^+$, [Ta(CH. .CMe_3)(L)Cl_3]$_2$, and Ti(CH_2-μ-H)Cl_3($Me_2PCH_2CH_2PMe_2$) (the values of r_A are in the range 0.59–0.69). The bridging interaction in Mn(η^3-MeC_6H_7-μ-H)$(CO)_3$, [Fe(η^3-C_8H_{12}-μ-H) {P(OMe_3)$_3$}$_3$]$^+$,

$Mo(COCH_2\text{-}\mu\text{-}H)(S_2CNMe_2)(CO)(PMe_3)_2$, $[Ir(PPh_3)_2(H)_2(N,C\text{-}8\text{-}methylquinoline)]^+$, and $Ti(CH_2CH_2\text{-}\mu\text{-}H)Cl_3(Me_2PCH_2CH_2PMe_2)$ are less strong (the values of r_A are in the range 0.75–1.0). The bridge bonds in the complexes $Mo[BEt_2(pyrazolyl)_2](CO)_2(\eta^3\text{-}C_3H_4Ph)$, $Pd(PhCH{=}NMe)_2Cl_2$, and $[M(PPh_2CMe_3)_2]_2$ (M = Pd or Pt), where r_A = 1.0–1.6, are weakest.

Table 3. M...H and C...H distances in complexes with a bridging hydrogen atom according to neutron diffraction data.

Compound	M...H distance, Å	r_M, Å	r_M+r_H, Å	C–H distance, Å	Refs.
$Ti(CH_2\text{-}\mu\text{-}H)(Dmpe)Cl_3$	2.447 (3)	1.56	1.93	1.095 (3)	[75]
$Ta(\eta\text{-}C_5Me_5)(CHCMe_3)(C_2H_4)PMe_3$	2.042 (5)	1.66	2.03	1.135 (5)	[84, 85]
$Th(\eta\text{-}C_5Me_5)_2(CH_2CMe_3)_2$	2.597 (9); 2.648 (9)	1.73	2.10	1.114 (9); 1.122 (8)	[83]
$[Ta(CHCMe_3)(PMe_3)Cl_3]_2$	2.119 (4)	1.66	2.03	1.131 (3)	[84, 85]
$Mn(\eta^3\text{-}MeC_6H_7\text{-}\mu\text{-}H)(CO)_3$	1.84 (1)	1.38	1.75	1.19 (1)	[95]
$[Fe(\eta^3\text{-}C_9H_{12}\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	1.874 (3)	1.34	1.71	1.164 (3)	[100, 101]
$Fe_4(\mu\text{-}CH)(H)(CO)_{12}$	1.753 (4)	1.34	1.71	1.191 (4)	[104]

Note. The average estimate of the covalent radius r_{Th} is based on Th–C bond lengths of 2.543(4) and 2.456(4) Å and the radius r_C = 0.77 Å.



The structure of the complex $(PMe_3)_2Ti(BH_4)_3$.[14]

In 1975–1982, Schrock and co-workers obtained a large number of electron-deficient niobium, tantalum, and tungsten complexes with alkylidene (carbene) ligands, namely :CH–CMe_3, :CH–Ph, etc.; the structurally characterised 14-electron and 16-electron complexes of this type are presented in Table 4, which includes also for comparison data for a series of 18-electron complexes. The following features of the coordination of the alkylidene ligands to the electron-deficient centre have been discovered. The character of the coordination (distances, angles) depends very strongly on whether the complex is of the 16-electron or 18-electron type. Alkylidene ligands contain an sp^2-carbon atom for which a trigonal-planar configuration with valence angles close to 120° is ideal. Deviations from the ideal geometry involving an increase in the $M-C_\alpha-C_\beta$ angles occur in both 16-electron and 18-electron complexes. However, the angles for the 18-electron complexes do not exceed 135 to 150°, whereas in the 16-electron complexes the distortion is significantly greater and the $M-C_\alpha-C_\beta$ angles are 160–170°. The $M-C_\alpha$ distances in the 18-electron complexes are 2.03–2.07 Å, while in the 16-electron complexes they are significantly smaller, amounting to 1.86–1.96 Å. In those cases where the locations of the hydrogen atoms have been determined and the M...H–C bridge fragments (carbene fragments) have been detected, the $M-C_\alpha-H$ angles are sharply diminished–from 90–110° to acute angles in the range 70–80°.

Table 4. Certain structural parameters of the carbene ligands :C(H)–CMe_3 and :C(H)–Ph in the 14-, 16-, and 18-electron tantalum and tungsten complexes.

Compound	Angles, deg		$M-C_\alpha$ distance, Å	$J(^{13}C-H)$, Hz	Refs.
	$M-C_\alpha-C_\beta$	M–C–H			
Formally 14- and 16-electron complexes					
$Ta(\eta\text{-}C_5Me_5)(CHCMe_3)(C_2H_4)PMe_3$	170.0	78.1	1.946	74	[85]
$Ta(CHCMe_3)_2(\eta\text{-}C_5Me_3H_2)(PMe_3)_2$	168.9 154.0	*	1.932 1.955	91 104	[120]
$Ta(\eta\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$	166.0	*	1.883	82	[121]
$[Ta(CHCMe_3)(PMe_3)Cl_3]_2$	161.2	84.8	1.898	101	[85]
$[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2$ (N_2)	160.3 158.5	*	1.937 1.932	91 [123]	[122]
$W(CHCMe_3)(CO)(PMe_3)_2Cl_2$	168.7	72.2	1.859	73	[91, 92]
$W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(Dmpe)$	150.4	*	1.942	90 [125]	[124]
$W(CHPh)(CO)(PMe_3)_2Cl_2$	164.6	74.6	1.860	82	[93]
18-electron complexes					
$Ta(\eta\text{-}C_5H_5)_2(CHCMe_3)Cl$	150.4	111	2.030	121	[126]
$Ta(\eta\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$	135.2	*	2.070	127	[127]
$Ta(\eta\text{-}C_5H_5)_2(CH_2)(CH_3)$	—	*	2.026	132	[128]
$W(CHPh)(PhC{\equiv}CPh)(PMe_3)_2Cl_2$	138	92.1	2.05	126	[93, 94]

*The locations of the hydrogen atoms have not been determined.

All the distortions in the geometry of the electron-deficient alkylidene complexes mentioned above have the same cause and are induced by the interaction of the α-hydrogen atom and the electrons of the C–H bond with the metal. Yet another parameter, which in the case of the carbene ligands :C(H)R depends greatly on whether the C–H hydrogen bond is of the bridge type, is the spin–spin coupling constant $^1J(^{13}C-H)$ for the ^{13}C NMR spectra. The constants for the C–H sp^3-bond are usually 120–125 Hz, while anomalously low values of the constant J, amounting to 50–110 Hz, are characteristic of the electron-deficient CHB (see below). This indicates a weakening (loosening) of the C–H bond when it is coordinated to the metal. The set of properties enumerated above constitutes characteristic features of the presence of M...H–C bridge 2e,3c-bonds.

An XRD study has been performed on the electron-deficient complexes $Mn_2(C_6H_{11})_4(Me_2PCH_2CH_2PMe_2)$,[129] $(\eta\text{-}C_5Me_5)_2ScCH_2CH_3$,[130] $(\eta^5\text{-}C_5Me_5)_2YCH_3.C_4H_8O$,[131] and also $(\eta^5\text{-}C_5Me_5)_2Th\overline{CH_2\text{-}(\eta^1{:}\eta^5\text{-}C_5R_2H_3)M}$ ($\eta^5\text{-}C_5R_2H_3$)Me, where M = Zr or Hf,[132] but, owing to the structural disorder in the crystal, it was not possible to reach clear-cut conclusions as to the presence or absence of an agostic hydrogen atom. For the same reason, it has not been possible to establish unambiguously whether the Co...H–C or the Co...H–B bond is formed in the complex $Co(\eta\text{-}C_5H_5)(\eta\text{-}Et_4C_2B_2CHMe)$.[133]

The possibility of the simultaneous coordination to the same metal atom of two bridging hydrogen atoms of the $M-CH_2$ fragment has been demonstrated in the complexes $Ti(\eta\text{-}C_5Me_5)(CH_2Ph)_3$ [79] and $Th(\eta\text{-}C_5Me_5)_2(CH_2CMe_3)_2$.[83] In these cases, there exist

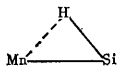
in the molecule both bridging and non-bridging CH_2 fragments whose parameters differ sharply. The M—C and C—H distances are significantly shorter precisely for the CH_3 group participating in the bridging interaction compared with the non-bridging CH_2 (Table 5).

Table 5. Structural data for complexes with two bridging hydrogen atoms.

Parameter	Method	Bridging CH_2 group	Non-bridging CH_2 groups
Ti (η-C_5Me_5) (CH_2Ph)$_3$ [79]			
Ti–C_α distance, Å	XRD	2.081 (10)	2 . (10); 2.140 (10)
Ti–H distance, Å	»	2.32 and 2.37	2.57—2 66
Ti–C_α–C_β angle, deg	»	139.0 (7)	114.0; 113.9
Th (η-C_5Me_5)$_2$ (CH_2CMe_3)$_2$ [83]			
Th–C_α distance, Å	ND	2.456 (4)	2.543 (4)
Th–H distances, Å	»	2 597 (9); 2.648 (9)	2.996 (9); 2.956 (9)
C_α–H distances, Å	»	1.114 (9); 1.122 (8)	1.079 (11); 1.095 (8)
Th–C_α–C_β angle, deg	»	158.2 (3)	132.1 (3)
Th–C_α–H angle, deg	»	84.1 (5); 87.1 (5)	104.2 (6); 101.1 (5)

Note. The numerals in square brackets denote references (Translator).

The formation of M...H—E 2e,3c-bonds by transition metals is not restricted to bonds with carbon alone. Whole series of cyclopentadienyl derivatives of manganese of the type $Mn(\eta\text{-}C_5H_5)(CO)_2\cdot(SiR_3)H$, in which there is a bridging hydrogen atom and the fragment



have been obtained and characterised structurally (Table 6). On passing from $SiCl_3$ to Si(Me) (naphthyl)Ph and $SiPh_3$, the Mn—Si and Mn—H distances increase somewhat, while the Si—H distances hardly change. The complexes $Ti(BH_4)_3(PR_2)_2$, where R = Me or Et, have been obtained recently. According to XRD data, the complex with PMe_3 contains two Ti...H...BH_3 2e,3c-bonds.[141] The molecule of this complex has the structure of a trigonal bipyramid with two PMe_3 ligands at the apical positions (see Figure). Of the three BH_4 groups in the equatorial plane, one is coordinated in the usual way, via two bridging H atoms [with the distances Ti—H = 1.90(7) Å, B(1)—H = 1.03(7) Å, and the non-bonding distance Ti...B(1) = 2.40(1) Å]. The other two BH_3 groups are linked to Ti by two three-centre Ti...H—B(2, 3) bonds involving one H atom from each BH_4 group: the distances Ti—B(2, 3) = 2.27(1) Å and Ti...H = 1.73(7) Å are shorter by 0.17 Å than in bonding of the type $Ti(\mu\text{-}H)_2B$. The distances from Ti to the other two H atoms in BH_3 are 2.25(7) and 2.68(7) Å, which exceeds by approximately 0.5 and 0.9 Å the distance to the bridging H atom. The M...H—B (where M = Mo, W, Fe, Ru, or Rh) bridge bonds are present in many transition metal complexes with carbaboranyl ligands of various types, which have been characterised by structural methods.[142-146]

V. THE STRUCTURE IN SOLUTIONS

The ^1H, ^{13}C, and ^{31}P NMR methods and in certain cases IR spectroscopy in the ν(C—H) frequency range are of principal importance for the identification and study of CHB in solutions. The hydrogen atoms of the CH_3, CH_2, and CH fragments involved in the bridge interaction with the metal give rise to ^1H NMR signals in strong fields (δ from 0 to -15 p.p.m.), i.e. in the region where there are signals due to terminal hydrido-ligands. It is therefore impossible to distinguish the two types of hydrogen atoms on the basis of ^1H NMR spectra. For the titanium, tantalum, and niobium complexes, where the metal atom has a small number of *d* electrons, the upfield shift of the signals due to the protons and ^{13}C nuclei in the M...H—CH_n fragments is usually weaker or is not observed at all. Anomalously low ^1J (^{13}D—H) constants for the ^{13}C NMR spectra, amounting to 50—110 Hz, are characteristic of the M...H—CH groups, which probably indicates a smaller strength of the C—H bridge bond compared with the usual bonds.

Table 6. Structural data for silylmetal hydride complexes with three-centre M...H—Si bonds.

Compound	Method	Distances, Å			Mn–H–Si angle, deg	Refs.
		Mn—H	Mn—Si	Si—H		
$Mn(\eta\text{-}MeC_6H_4)(CO)_3(SiCl_3)(\mu\text{-}H)$	XRD	1.47 (3)	2.254 (1)	1.79 (4)	—	[134]
$Mn(\eta\text{-}C_6H_5)(CO)_2(SiCl_2Ph)(\mu\text{-}H)$	XRD	1.49 (6)	2.310 (2)	1.79 (6)	—	[136]
$Mn(\eta\text{-}C_6H_4Me)(CO)_2(SiFPh_2)(\mu\text{-}H)$	ND	1,569 (4)	2.352 (4)	1 802 (5)	88	[135], [136]
$Mn(\eta\text{-}C_6H_4Me)(CO)(L)(SiHPh_2)(\mu\text{-}H)$ (L = PMe_3)	XRD	1.49 (4)	2.327 (1)	1 78 (4)	91	[136]
$Mn(\eta\text{-}C_6Me_5)(CO)_2(SiHPh_2((\mu\text{-}H)$	XRD	1.52 (3)	2.395 (1)	1.77 (3)	93	[136]
$Mn(\eta\text{-}C_5H_5)(CO)_2(SiPh_3)(\mu\text{-}H)$	XRD	1.55 (4)	2.424 (2)	1.76 (4)	—	[137]
$Mn(\eta\text{-}C_6H_4Me)Mn(CO)_2(SiR_3)(\mu\text{-}H)$ [SiR_3 = Si(Me)(Ph)(α-naphthyl)]	XRD	—	2,461 (7)	—	—	[138]
$Mn(\eta\text{-}MeC_5H_4)(CO)\times$ $\times(Ph_2PCH_2CH_2SiMe_2\text{-}\mu\text{-}H)$	XRD	1.53 (4)	2,547 (2)	1.75 (4)	97	[139]
$Cr(\eta\text{-}C_6Me_6)(CO)_3(SiPh_2H)(\mu\text{-}H)$	XRD	1.61 (4)	2.456 (1)	1,61 (4)	—	[140]

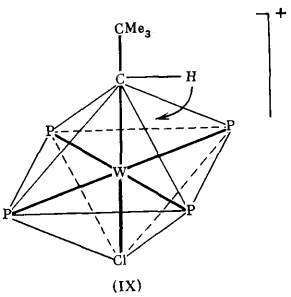
It follows from the XRD data (Table 2) that the C—H bonds coordinated to the metal in the CHB are extended and the hydrogen atom is close to the metal. The extension of the C—H bond weakens it and reduces the force constant of the C—H stretching vibration. The ν(C—H) frequencies for the bridging hydrogen in the CHB are 2200—2700 cm^{-1}, which is lower by 100—600 cm^{-1} than the usual value (2800—3000 cm^{-1}). The low constant $J(^{13}C—H)$ and the sharp decrease in the ν(C—H) frequencies indicate fairly reliably a decrease in the C—H bond orders on coordination to the metal. Both these effects are distinct in the NMR and IR spectra of the 14-electron and 16-electron alkylidene complexes of niobium, tantalum, and tungsten with the :CH—CMe_3 and :CH—Ph ligands and also the related angular sandwich complexes of titanium and thorium (Table 7). Several alkylidene complexes of tantalum and tungsten have been characterised structurally (Table 4) and bridging hydrogen atoms have been found in them. On the basis of the similar $J(^{13}C—H)$ constants and ν(C—H) frequencies, presumably the other complexes listed in Table 7 also have a distorted geometry with the α-hydrogen atom inclined relative to the metal and involving the formation of M...H—C bridge bonds.

Table 7. The constants $J(^{13}C-H)$ and the frequencies $\nu(C-H)$ of complexes with M...H−C bridge bonds.

Compound	$J(^{13}C-H)$, Hz	$\nu(C-H)$, cm^{-1}	Refs.
$Y(\eta\text{-}C_5Me_5)_2N(SiMe_3)(SiMe_2CH_2\text{-}\mu\text{-}H)$	116	—	[68]*
$Y(\eta\text{-}C_5Me_5)_2C\text{-}\mu\text{-}H(SiMe_3)(SiMe_2CH_2\text{-}\mu\text{-}H)$	84	—	[68]*
$Y(\eta\text{-}C_5Me_5)_2CH_2\text{-}\mu\text{-}H\cdot C_4H_8O$	108	2770	[131]*
$Sc(\eta\text{-}C_5Me_5)_2R$			
R=Me	111	—	[130]*
R=Et	122	2593, 2503, 2440	[130]*
R=Pr	117	—	[130]
$Nd(\eta\text{-}C_5Me_5)_2C\text{-}\mu\text{-}H(SiMe_3)_2$	90	—	[147]*
$TiMe_{1.3}Cl_{0.7}(Dmpe)_2$	—	2750	[78]*
$TiCp_2(CH_2\text{-}\mu\text{-}H)(\mu\text{-}CH_2)Rh(C_8H_{12})$	88	2460	[77]*
$[Hf(\eta\text{-}C_5Me_5)Cl{-}\mu\text{-}(CHCH_2CMe{=}CMeCH_2)]_2$	94	—	[82]*
$Hf(\eta\text{-}C_5Me_5)(C_8H_{10})R$			
R=Me	112	—	[148]
R=Et	121	2600, 2500, 2440	[148]
$R=CH_2CMe_3$	104	—	[148]
$Th(\eta\text{-}C_5Me_5)_2(CH_2SiMe_3)Cl$	104	—	[83]
$Th(\eta\text{-}C_5Me_5)_2(CH_2SiMe_3)_2$	99	—	[83]
$Th(\eta\text{-}C_5Me_5)_2(CH_2CMe_3)_2$	97	—	[83]*
$Th(\eta\text{-}C_5Me_5)_2\overbrace{CH_2{-}(\eta^1{:}\eta^5\text{-}C_5H_5)}M(\eta\text{-}C_6H_5)$			
M=Zr	89	—	[132]
M=Hf	84	—	[132]*
$Ta(\eta\text{-}C_5Me_5)(=CHCMe_3)(C_2H_4)PMe_3$	74	2605	[84, 85]*
$[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$	101	2520	[84, 85]*
$Ta(=CHCMe_3)(CH_2CMe_3)_3$	90	—	[149]
$Nb(=CHCMe_3)(CH_2CMe_3)_3$	101	—	[149]
$Ta(=CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$	98 and 96	—	[150]
$Ta(\eta\text{-}C_5H_5)(=CHCMe_3)_2(PMe_3)$	97 and 90	—	[150]
$Ta(\eta\text{-}C_5H_5)(=CHCMe_3)(X)(Y)$	76—84	2420—2525	[151]
X, Y = Cl, Br, Me, CH_2CMe_3			
$M(=CHR)L_2X_3$, M = Nb, Ta, R = alkyl, Ph; L = phosphine, X = Cl, Br	70—100	2400—2700	[152]
$Ta(=CHCMe_3)(PMe_3)_2(Cl)(H)$	72	2440	[153]
$Ta(\eta\text{-}C_5Me_5)(=CHCMe_3)(PMe_3)(Cl)H$	72	2525	[153]
$Ta(=CHCMe_3)(PMe_3)_4Cl$	69	2200	[153]
$Ta(\eta\text{-}C_5H_5)(=CHPh)(X)(Y)$	82—91	—	[121]
X, Y = Cl or CH_2Ph			
$Ta(=CHCMe_3)(Dmpe)_2Cl$	57	2200	[154]
$Ta(=CHCMe_3)(C_2H_5)(PMe_3)_2Cl_2$	80	—	[155]
$W(=CCMe_3)(=CHCMe_3)(CH_2CMe_3)(Dmpe)$	90	—	[125]*
$W(=CHCMe_3)(PMe_3)_2Cl_3(H)$	84	2395	[91]
$W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$	73	—	[91, 92]*
$W(=CHCMe_3)(C_2H_4)(PMe_3)_2Cl_2$	70	—	[91]
$W(=CHPh)(CO)(PMe_3)_2Cl_2$	83	—	[93, 94]*
$W(CO)_3[P(C_6H_{11})_3]_2$	—	2552	[90]*
$W(\eta\text{-}C_6Me_5)Me_3(=CH_2)$	110	—	[156]
$Mn_2(CH_2R)_4L_2$ R = $SiMe_3$, CMe_3, Ph; L = PMe_3, $PMePh_2$	—	2700—2772	[99]*
$Fe_3(\mu\text{-}H)_2(CO)_9\text{-}\mu^3\text{-}(CH\text{-}\mu\text{-}H)$	89	—	[67]
$Fe_3(\mu\text{-}H)(CO)_9\text{-}\mu^3\text{-}(CH\text{-}\mu\text{-}H_2)$	98	—	[67]
$[Fe_3(\mu\text{-}H)(CO)_9\text{-}\mu^3\text{-}(CH\text{-}\mu\text{-}H)]^-$	60	—	[67]
$[Mn(\eta\text{-}C_5H_7\text{-}\mu\text{-}H)(Me_2PCH_2)_3CMe]^+$	118	2300—2360	[166]

*The structure has been established by structural methods.

On protonation (with CF_3SO_3H or CF_3COOH), the 18-electron carbyne complex $L_4(Cl)W{\equiv}CCMe^3$ is converted into the cationic 16-electron carbene complex $[L_4(Cl)W{=}CH{-}CMe_3]^+$ (IX) (L = PMe_3 throughout), in which the α-hydrogen atom of the carbene ligand interacts with one of the C−P−P faces of the octahedron and the W atom:[157]



(IX)

The spectroscopic data for compound (IX) and the isoelectronic neutral complex $L_4(Cl)Ta{=}CH{-}CMe_3$ (X)[153] are similar:

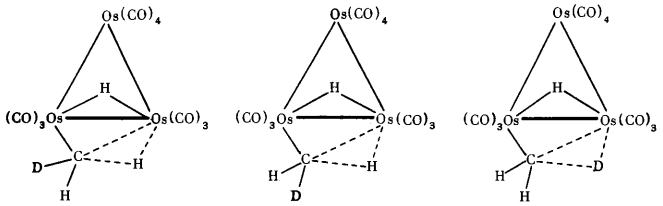
Compound	δ(CH) at 295 K, p.p.m.	$J(H-^{31}P)$, Hz	$J(^{13}C-H)$, Hz	Refs.
$[L_4(Cl)W{=}CH{-}CMe_3]^+$	−8.4 (quintet)	9	45	[157]
$L_4(Cl)Ta{=}CH{-}CMe_3$	−7.4 (quintet)	6	69	[153]

The complexes (IX) and (X) are stereochemically non-rigid compounds but at 295 K the rapid, in terms of the NMR time scale, migration of H between the four C−P−P faces leads to the apparent equivalence of the four P atoms.

In the 16-electron cations $[L_4(X)W{=}CH_2]^+$, where X = Cl[157] or I,[158] formed on protonation of the carbyne complexes $L_4(X)W{\equiv}CH$, at 298 K both hydrogen atoms of the methylene ligand give rise to a single averaged signal owing to rapid exchange (δ = −0.16 and −0.80 p.p.m.), which is split into a quintet. On cooling to 165 or 153 K, the two H atoms become non-equivalent and give rise to two different signals: the shifts δ are −7.67 and −9.00 p.p.m. for the H atoms interacting with the C−P−P face and the W atom; for the compound with X = Cl, the H atom not interacting with W produces a signal at δ = 7.05 p.p.m., while in the case where X = I the signal of this H atom is masked by the signal of the solvent. The complex with X=I has been studied by XRD, but the locations of the H atoms have not been determined.[159]

The majority of the CHB contain the CH_3 or CH_2 groups and are stereochemically non-rigid complexes (see below), whose NMR spectra exhibit reversible temperature variations (TV). Under the conditions of rapid exchange, the two or three protons of the CH_3 or CH_2 groups are equivalent and give rise to an average signal in the range δ = 0−−3 p.p.m., while the carbon nucleus in the ^{13}C NMR spectra is manifested by a binomial 1:2:1 triplet or a 1:3:3:1 quartet with an average constant J = 120−130 Hz. In slow exchange, the two protons of the CH^aH^b group are non-equivalent, form the AB (or AX) system, and give rise to two doublets with a geminal constant $J(H,H)$ = 15−30 Hz. The three non-equivalent protons in $CH^aH^bH^c$ form the ABC three-spin system and give rise to three multiplets, the signal of the bridging proton (H^a) usually having δ = −10−−15 p.p.m. The resonance signal of the carbon nucleus is split under the conditions of slow exchange respectively into a doublet of doublets (for CH^aH^b) or into a doublet of triplets ($CH^aH^{b,c}$) with different constants: $J(^{13}C-H^a)$ = 50−110 Hz for the bridging H^a atom and J = 130−150 Hz for the non-bridging H^b and H^c atoms. The ^1H and ^{13}C NMR data for CHB under the conditions of both rapid and slow exchange are compiled in Table 8.

When H is replaced by D in the M...H−CH_n (n = 1,2) groups, additional effects appear in the ^1H and also ^2H NMR. Deuteriation leads to an unusual upfield shift of the resonance signals of the CH_2D, CHD_2, and CHD groups relative to CH_3 and CH_2 (Δδ = 0.3−1.2 p.p.m.), although for the usual compounds geminal substitution of H by D in CH_3 or CH_2 is accompanied by only a very slight shift of the signals (Δδ = 0.01−0.3 p.p.m.). An appreciable influence of the H/D substitution on the constants $J(^{13}C-H)$ has been noted. The marked dependence of δ and Δδ on isotope substitution was first observed for the cluster complex $HOs_3(CO)_{10}\cdot(CH_2\text{-}\mu\text{-}H)$ and has been called the "isotope perturbation effect" or the chemical shift effect.[161] Three rotational isomers are possible for this cluster, in which the bridge position is occupied by either H [rotational isomers (XI) and (XII)] or by D [compound (XIII)]:



(XI) (XII) (XIII)

The equilibrium (XI) ⇄ (XII) ⇄ (XIII), whose position depends on temperature, exists in solution; the contributions of the individual rotational isomers are not the same and the distribution differs from the statistical distribution owing to the difference between the properties of H and D (isotope effect). Since the C–H and C–D bridge bonds are extended compared with the non-bridge bonds and also bearing in mind the difference between the zero-point energies of the C–H and C–D bonds, one may conclude that the bridge position is preferred for the light H atom compared with the heavier D atom. Each of the H-bridged forms will therefore contribute more than the D-bridged form.

Since the H atom linked to two M atoms should generate a signal in a stronger field than the non-bridging atom, for unequal amounts of the individual rotational isomers the signal due to the protons in CH_2D is located in a stronger field than the signal from CH_3. The observed strong temperature dependence of δ and Δδ is associated with the shift of the equilibrium between the rotational isomers. Data for the dependence of the chemical shifts on isotope substitution in CHB are presented in Table 9.

Table 8. ^1H and ^{13}C NMR data for complexes with bridging hydrogen atoms.

Compound	Group	^1H NMR spectra: rapid exchange		^1H NMR spectra: slow exchange			^{13}C NMR spectra				Refs.
		T, °C	δ(H), p.p.m.	T, °C	δ(H^a), p.p.m.	δ(H^b and H^c), p.p.m.	T, °C	δ(^{13}C), p.p.m. (multiplicity*)	J(^{13}C–H), Hz (H^a)	J(^{13}C–H), Hz (H^b and H^c)	
$Ti(CH_2\text{-}\mu\text{-}H)(Me_2PCH_2CH_2PMe_2)Cl_3$	CH_3	–90	2.29	—	—	—	–90	87.5 (q)	129.5		[75]
$Ti(Cp)_2(CH_2\text{-}\mu\text{-}H)(\mu\text{-}CH_2)Rh(C_8H_{12})$	CH_3	25	–3.13	–90	–12.15	1.28	–90	51.1 (dt)	88	127	[77]
$Ta(\eta^5\text{-}C_5R_3(CH_2CMe_2CH_2)_2)Cl_2$	CH_2	—	—	–70	0.33	4.03	—	—	—	—	[86]
$Cr(\eta^5\text{-}C_6H_{10}\text{-}\mu\text{-}H)(PF_3)_3$	CH_2	—	—	–50	–12.58	–0.09	–80	1.9 (dd)	88	144	[63]
$Cr(\eta^4\text{-}C_7H_{11}\text{-}\mu\text{-}H)(CO)_2P(OMe)_3$	CH_3	–33	–3.75	–148	–10.03	0.12 and –1.58	—	—	—	—	[57]
$Cr(\eta^4\text{-}1,3\text{-cyclo-}C_7H_9\text{-}\mu\text{-}H)(CO)_3$	CH_2	–33	–4.27	–143	–10.10	1.88	–33	26.43 (dd)	110	134	[58]
$Cr(\eta^4\text{-}1,3\text{-cyclo-}C_7H_9\text{-}\mu\text{-}H)(CO)_2PMe_3$	CH_2	–33	–5.67	–148	–10.66	1.70	–33	25.51 (dd)	107	133	[58]
$Cr(\eta^4\text{-}1,3\text{-cyclo-}C_7H_9\text{-}\mu\text{-}H)(CO)_2P(OMe)_3$**	CH_2	–33 –33	–5.04 –3.48	–148	–11.06 –10.86	1.84 1.64	–33 –33	25.63 (dd) 27.68	104 108	132 132	[58] [58]
$[Mo(\eta^3\text{-}CH_2CHCHCH_2\text{-}\mu\text{-}H)(C_6H_6)(PMe_3)_2]^+$	CH_3	23	–3.05	–90	–9.16	0.8 and –0.8	–90	–3.9 (dt)	84	144	[32]
$Mo(\eta^3\text{-}C_3H_5)_3(CHMeCH_2\text{-}\mu\text{-}H)$	CH_3	–50	–2.90	–120	–8.43	0.5 and –0.9	–60 –115	7.3 (q) 7.3 (dt)	122 88	138	[160]
$WRe(\mu\text{-}CHR\text{-}\mu\text{-}H)(Me_2PCH_2PMe_2)(CO)_7$	CH_2	—	—	–20	–3.69	3.25	–20	18.2 (dd)	81	131	[33]
$Mn(\eta^3\text{-}C_6H_9\text{-}\mu\text{-}H)(CO)_3$	CH_2	–9	–5.7	–99	–12.8	1.6	–100	14.0 (dd)	85	146	[35]
$Mn(\eta^3\text{-}CH_2CHCMeCH_2\text{-}\mu\text{-}H)(CO)_3$***	CH_3 CH_3	25 25	–4.4 –4.2	–100 –100	–12.0 –11.8	0.4 and –1.4 – and –1.3	–90 –90	–4.7 (dt) 0.5	89 —	139 —	[59] [59]
$Mn(\eta\text{-}C_{15}H_{23})(CO)_3$	CH_3	25	–4.27	–80	–11.82	0.19 and –1.37	—	—	—	—	[97]
$Mn_2(\mu,\ \eta\text{-}C_{10}H_{16})(CO)_6$	CH_3	25	–4.42	–80	–12.42	–0.9 and –2.2	—	—	—	—	[97]
$[Mn(\eta^5\text{-}C_5H_7\text{-}\mu\text{-}H)(Me_2PCH_2)_2CMe]^+$	CH_3	–30	–6.23	–130	–15.31	–0.3 and –3.0	–30	35.9 (q)	118		[166]
$[Fe(\eta^3\text{-}CH_2CHCHCH_2\text{-}\mu\text{-}H)(CO)_3]^+$	CH_3	–19	–4.7	–80	–14.6	1.0 and –1.0	–80	–3.0 (dt)	74	146	[21, 25]
$[Fe(\eta^5\text{-}C_5H_9\text{-}\mu\text{-}H)(CO)_3]^+$	CH_2	–15	–6.5	–86	–15.0	2.0	25	24.6 (dd)	78—88	130—140	[25]
$[Fe(\eta\text{-}CH_2CHCHCH\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	CH_3	22	–5.92	–95	–15.2	–2.0 and –2.4	35 –120	–5.4 (t) –3.9 (dd)	129 100	140	[41]
$[Fe(\eta^3\text{-cyclo-}C_7H_{10}\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	CH_2	22	–7.14	–80	–15.77	1.2	35 –80	5.0 (t) 7.3 (dd)	130 80	140	[41]
$[Fe(\eta^5\text{-}C_9H_4\text{-}\mu\text{-}H)(CO)_3]^+$	CH_2	—	—	–85	–11.16	3.45	–90	9.0 (dd)	81	191	[24]
$[Fe_2(\mu\text{-}CH_2\text{-}\mu\text{-}H)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$	CH_3	0	–1.88	—	—	—	0	23.4	120		[39]
$[Fe_3(\mu\text{-}H)_3(\mu\text{-}CH\text{-}\mu\text{-}H)(CO)_9]^-$	CH_2	—	—	–60	–10.1	6.6	–80	118.5 (dd)	67	155	[67]
$[Ru(\eta^3\text{-}C_8H_{13}\text{-}\mu\text{-}H)(P(OMe)Ph_2)_3]^+$	CH_2	34	–1.89	–80	–5.15	0.15	30	27.4	—	—	[44]
$[Ru(\eta^3\text{-}C_7H_{10}\text{-}\mu\text{-}H)(P(OMe)Ph_2)_3]^+$	CH_2	—	—	–90	–8.2	1.5	–20	18.1	—	—	[62]
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–10.13	–0.09	–80	2.52 (dd)	78	159	[45]
$[Os(\eta\text{-}C_6H_3Me_3)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–10.08	0.10	–80	–3.30 (dd)	66	160	[45]
$[Co(\eta\text{-}C_6Me_4Et)(\eta\text{-}CH_2{=}CH_2)(CH_2CH_2H)]^+$	CH_3	—	—	–80	–12.1	1.48 and 0.46	–90	26.6	67	155	[49]
$[Co(\eta\text{-}C_5Me_5)(CH_2CH_2\text{-}\mu\text{-}H)P(C_6H_4Me)_3]^+$	CH_3	–20	–4.94	–80	–12.67	–0.5 and –1.8	–80	–5.92	66	146	[50]
$[Co(\eta\text{-}C_5Me_5)(CH_2CHR\text{-}\mu\text{-}H)P(OMe)_3]^+$	CH_3	—	—	–70	–12.1	–0.1 and –0.2	–90	–5.8	61	152	[51]
$[Co(\eta\text{-}C_5Me_5)(CH_2CH_2\text{-}\mu\text{-}H)PPhMe_2]^+$	CH_3	25	–4.32	–85	–12.4	–0.13 and –0.55	—	—	—	—	[52]
$[Rh(\eta\text{-}C_5H_5)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–7.63	0.65	–80	2.20 (dd)	81	159	[45]
$[Rh(\eta\text{-}C_5Me_5)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–6.83	0.41	–80	6.10 (dd)	83	152	[45]
$[Ir(\eta\text{-}C_5Me_5)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–9.53	0.22	–80	9.02 (dd)	50	165	[45]
$[Ir(PPh_3)_2(H)_2(N,C\text{-}8\text{-methylquinoline})]^+$	CH_3	–43	1.1	—	—	—	—	–8.15	—	—	[60]

*Here q = quartet, dd = doublet of doublets, and dt = doublet of triplets.

**The complex is chiral and exists as a mixture of two diastereoisomers.

***Two isomers with different positions of the bridging H atom.

It has been suggested that there is a possibility of the coordination of the metal centre to the CH_4 molecule, which is isoelectronic with the BH_4^- anion, and also to other alkanes.[141] In a study of the photochemical reactions of the complexes $(\eta\text{-}C_5R_5)M(CO)_2$ (where R = H or Me; M = Co, Rh, or Ir) in matrices at 12 K by IR and UV spectroscopic methods, the formation of products of the oxidative addition of CH_4, and, furthermore, the formation of compounds of yet another type, for which the structure of complexes with an agostic hydrogen atom was proposed, i.e. $(\eta\text{-}C_5R_5)(CO)$. .M...H$-CH_2$, was noted.[162] In a number of investigations, the formation in solutions of CHB of different structure, containing Ta,[163] W,[164] Fe,[165] Mn,[166] Ru,[167,168] and Co,[169] has been observed or postulated on the basis of NMR, IR, and UV spectroscopic data as well as kinetic data.

Table 9. Dependence of the chemical shifts δ in the ^1H NMR spectra on isotope substitution.

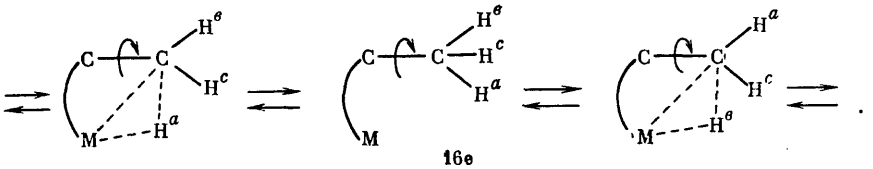
Compound	Group	δ, p.p.m.			Refs.
		CH_3	CH_2D	CHD_2	
$TiCl_3(Dmpe)(CH_2\text{-}\mu\text{-}H)$	CH_3	2.29	1.89	—	[75]
$[Mo(C_4H_6)(\eta\text{-}C_6H_4CH_2\text{-}\mu\text{-}H)(PMe_3)_2]^+$	CH_3	−3.05	−3.66	—	[32]
$[Fe_2(CO)_3(\mu\text{-}CO)(\mu\text{-}CH_2\text{-}\mu\text{-}H)(\eta\text{-}Cp)_2]^+$	CH_3	−1.88	−2.62	—	[39]
$[Fe_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(CH_2\text{-}\mu\text{-}H)Cp_2]^+$	CH_3	−2.90	−3.47	—	[42]
$[Ir(\eta\text{-}CH_2CMeCMeCH_2\text{-}\mu\text{-}H)(PPh_3)_2(H)]^+$	CH_3	−2.23	−2.54	−2.91	[55]
$[Ir(N,C\text{-}\mu\text{-}H\text{-}8\text{-methylquinoline})(PPh_3)_2N_2]^+$	CH_3	1.10	0.96	0.82	[60]
$Os(H)(CO)_{10}(CH_2\text{-}\mu\text{-}H)$	CH_3	−3.67	−4.02	−4.41	[161]
$Fe_3(CO)_9(\mu\text{-}H)(\mu^3\text{-}HC\text{-}\mu\text{-}H_2)$	CH_3	−8.49	−8.78	−9.05	[67]
		CH_2	CHD		
$[W(Cl)(PMe_3)_4(=CH\text{—}H)]^+$	CH_2	−0.16	−1.40		[157]
$Mn(\eta\text{-}C_9H_9\text{-}\mu\text{-}H)(CO)_3$	CH_2	−5.8	−7.0		[35]
$[Fe(\eta\text{-}C_8H_{12}\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	CH_2	−6.5	−7.6		[41]

VI. PROPERTIES AND REACTIVITY

1. Stereochemical Non-rigidity

The majority of CHB are stereochemically non-rigid complexes characterised by different intramolecular rearrangements (IAR) associated with the migration of a hydrogen atom and/or ML_n fragments relative to the carbon atom of the skeleton of the η-ligand. These rearrangements can be degenerate (DIAR) or non-degenerate. Several (up to three) different IAR can occur simultaneously, whereupon the ^1H, ^{13}C, and ^{31}P NMR spectra exhibit reversible temperature variations. The following types of rearrangements with participation of the CH_3, CH_2, CH groups and ML_n fragments are typical for CHB.

1. The interchange of the positions of the bridging H^a and non-bridging H^b and H^c atoms in the CH_3 group (rotation about the $C-CH_2-\mu$-H bond) via a 16-electron intermediate—a type "A" rearrangement:

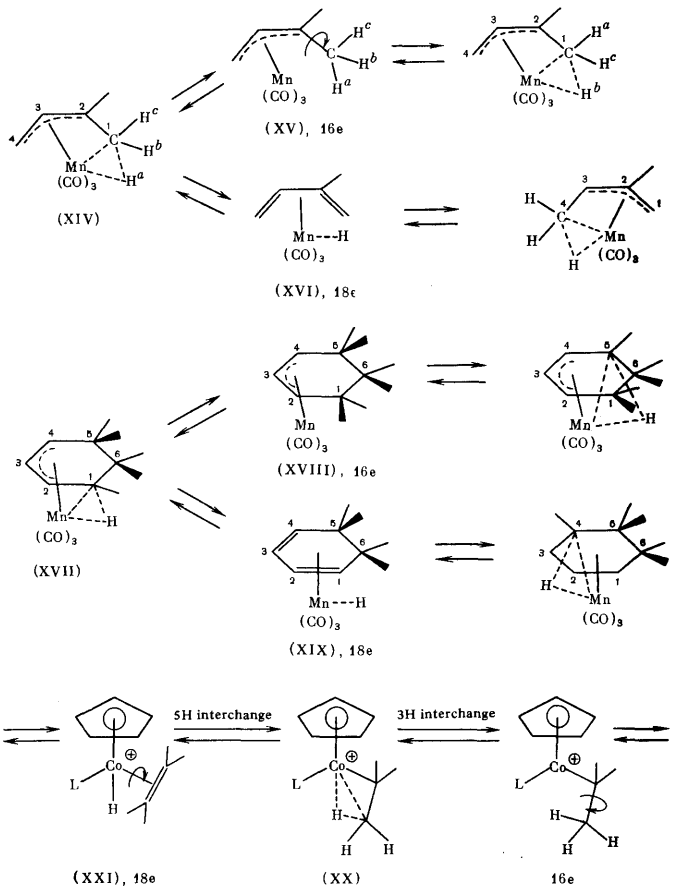


16e

The positions of the C atoms do not then change.

2. Two types of rearrangements, illustrated in relation to manganese compounds[35,59] (Scheme 4), are possible for η^3-allyl CHB.

Scheme 4



After the dissociation of the bridge bond, the μ-H atom can move either to a carbon atom with formation of the 16-electron intermediates (XV) and (XVIII) or to the metal atom with formation of 18-electron dienemetal hydride intermediates (XVI) and (XIX). For the non-cyclic CHB (XIV), the rearrangement via the 16-electron intermediate (XV) belongs to type "A" and leads to the exchange of the three protons H^a, H^b, and H^c. The rearrangement via the 18-electron intermediate (XVI) is non-degenerate owing to the presence of the methyl group at C(2) and leads to the exchange of the bridging hydrogen atom between the C(1) and C(4) atoms in the same ligand (a type "B" rearrangement).

For the cyclic CHB (XVII), rotation about the C−C bond is impossible and, after the formation of the 16-electron compound (XVIII), the bridging H atom is exchanged between C(1) and C(5) without change in the carbon skeleton (IAR) of type "B". The

rearrangement of compound (XVII) via the 18-electron intermediate (XIX) also leads to the migration of the bridge, but, in contrast to the rearrangement via the 16-electron intermediate, is accompanied by the 1,2-migration of $Mn(CO)_3$ relative to the carbon skeleton of the η-ligand. In a more general sense, all the IAE associated with the migration of ML_3 relative to the carbon skeleton of the ligand (rearrangements of type "C") can be assigned to this type.

In compounds (XVI) and (XIX) and analogous intermediates, the proton involved in the M—H bond is "acid" and readily enters into an exchange with the acid derived from the solvent. If the CHB are generated by treatment with deuterio-acids (Table 1), then deuterium is inserted under these conditions in the 1,4-positions for the non-cyclic system and in the 1,5-positions for the cyclic system.[41]

3. The cobalt complexes with the η^2-ethylene ligands (η-Cp)Co.(L)(η-CH_2=CHR), where L = phosphine, phosphite, or CH_2 = CH_2, produce on protonation the CHB $[(\eta\text{-Cp})Co(L)(CH_2CHR-\mu\text{-H})]^+$ (XX), where R = H or alkyl.[49–52] In this case, a type "A" rearrangement takes place (exchange of the three protons in $CH_2-\mu$-H) and also an IAR with the exchange of the five protons in $CH_2CH_2-\mu$-H via the intermediate (XXI) (Scheme 4) and rotation about the cobalt—ethylene bond (rearrangement of type "D").

4. Rearrangements associated with the interchange of the positions of the groups L in the ML_3 "tripod" (IAR of type "E") take place in CHB with the groups ML_3 = $Mn(CO)_3$, $Fe(CO)_3$, $Fe(P)_3$, $Ru(P)_3$, etc., where (P) = phosphite or phosphine.

5. In CH_3 having two or more identical structural elements (M atoms, C_2H_4 or C_4H_6 ligands, etc.) rearrangements take place with migration of the bridge between such elements (IAR of type "F"). The migration of μ-CH between two out of the four Fe atoms in $HFe_4(CO)_{12}(CH)$[43,104] as well as the alternate involvement of each of the four carbon atoms of the CH_2= groups of the protonated form $[Mo(PMe_3)_2(CH_2$=$CHCH$=$CH_2)_2H]^+$ in the formation of the Mo...H—C bond via an 18-electron metal hydride intermediate[32] are examples of such rearrangements. The migration of an α-hydrogen atom of the alkylidene ligand between the four C—P—P faces in the octahedral cationic complexes $[W(PMe_3)_4(X)(=CH-R)]^+$, where R = CMe_3 or H, can be assigned to IAR of type "F".[157] Apart from the rearrangement indicated, in the complex with R=H there is also a rearrangement involving the interchange of the positions of the two hydrogen atoms of the CH_2 ligand (type "B").

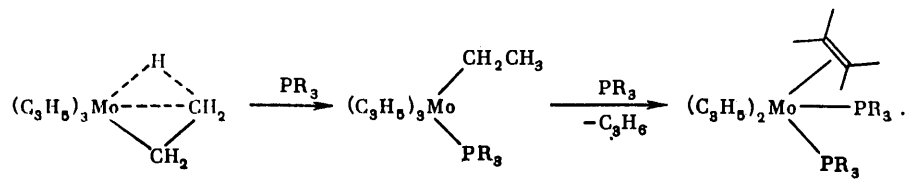
The rearrangements known for the CHB and the barriers $\Delta G^{\neq}$ obtained from the NMR data are listed in Table 10.

The chemical properties of the CHB have been little investigated. Their characteristic reaction involves the ready dissociation of the bridge bond. The M...H—C interaction is comparatively weak: on treatment with nucleophiles—the 2-electron ligands PR_3, $P(OR)_3$, CO, CNR, etc.—these bonds are readily cleaved with substitution of H by L, as shown below for tris-η^3-allylmolybdenum complexes:[160]

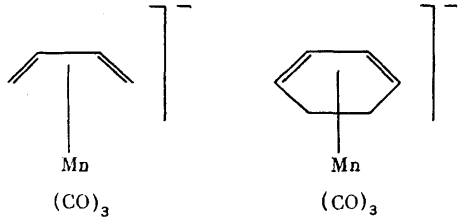
Table 10. Intramolecular rearrangements in complexes with three-centre M...H—C bonds.

Compound	Type of re-arrange-ment	ΔT, K	$\Delta G^{\neq}$, kJ mol^{-1}	Refs.
$Ti(Cp)_2(CH_2)(CH_2$-μ-H)$Rh(\eta\text{-}C_8H_{12})$	A	233 (T_c)	40.9	[77]
$Cr(\eta^4\text{-}C_7H_{11}$-μ-H)$(CO)_2P(OMe)_3$	A	124—240	28.6 (200 K)	[57]
	C	240—390	68.1 (300 K)	[57]
$Cr(\eta\text{-cyclo-}C_7H_{10}$-μ-H)$(CO)_2$(L)				
L = CO	B	125—240	27.9 (165 K)	[58]
	C	240—380	67.2 (350 K)	[58]
L = PMe_3	B	125—240	28.6 (165 K)	[58]
	C	240—380	64.1 (350 K)	[58]
L = $P(OMe)_3$	B	125—240	28.4 (165 K)	[58]
	C	240—380	61.4 (350 K)	[58]
$Cr(\eta\text{-}C_8H_{10}$-μ-H)$(PF_3)_3$	B	193—293	—	[63]
$[Mo(\eta\text{-}C_4H_8)(\eta\text{-}C_5H_4CH_2$-μ-H)$(PMe_3)_2]^+$	A	183—298	37.2	[32]
	F	183—298	77.2 and 81.0	[32]
$Mo(\eta^3\text{-}C_3H_5)_3CH(Me)CH_2$-μ-H	A	153—243	—	[160]
$[W(PMe_3)_4(Cl)$=$CHCMe_3]^+$	F	153—295	41.8	[157]
$[W(PMe_3)_4(Cl)$=$CH_2]^+$	F	165—298	—	[157]
$Mn(\eta^3\text{-cyclo-}C_6H_8$-μ-H)$(CO)_3$ (XVII)	B	174—264	34.6	[35]
	E	233—313	54.9	[35]
	F	281—392	65.0	[35]
$Mn(\eta\text{-}CH_2CHMeCH_2$-μ-H)$(CO)_3$ (XIV)	A	173—273	37.2	[59]
	B	323—384	72.2	[59]
$Mn(\eta\text{-}C_{15}H_{23})(CO)_3$	A	195—298	43.5	[97]
$Mn_2(\eta\text{-}C_{10}H_{16})(CO)_6$	A	195—298	41.7	[97]
$[Mn(\eta^5\text{-}C_5H_7$-μ-H)$(Me_2PCH_2)_3CMe]^+$	A	143—243	39.6	[166]
	B	243—303	69.0	[166]
	E	203—293	47.5	[166]
$[Fe(\eta$-enyl)$(P(OMe)_3)_3]^+$				
Enyl = cyclohexenyl	B	183—308	41.8	[41]
	E	183—308	66.5	[41]
Enyl = cycloheptenyl	B	183—308	44.0	[41]
	E	183—308	70.0	[41]
Enyl = cyclo-octenyl	B	123—273	21	[41]
	E	183—308	59.9	[41]
$[Ru(\eta^3$-Enyl$)(P)_3]^+$				
Enyl = butenyl	A	183—298	—	[62]
Enyl = cyclohexenyl, cycloheptenyl	B, C	183—298	—	[62]
	E			
$[Co(\eta^5\text{-}C_5H_4R)(\eta^3\text{-}C_2H_4)(CH_2CH_3$-μ-H)$]^+$	A	183—298	43.0	[49]
	D	183—298	51.1	[49]
$[Co(\eta^5\text{-}C_5Me_5)(P(C_6H_4Me)_3)(CH_2CHR$-μ-H)$]^+$	A	193—298	38.4	[51, 52]
	D	193—298	56.0	[51, 52]
$[Ir(PPh_3)_2(\eta^3\text{-}CH_2CMeCMeCH_2$-μ-H)H$]^+$	A, B	153—298	—	[55]

Depending on the type of complex and the nature of M, the ease of the dissociation of the bridge bond can be various. Thus $[Fe(\eta\text{-}C_8H_{12}$-μ-H$)\{P(OMe)_3\}_3]^+$ reacts with CO and $CNCMe_3$ but not with $P(OMe)_3$, the Fe...H—C bond being dissociated and the Fe—C_8H_{11} bond being retained.[41] On the other hand, the complexes $[Ru(C_8H_{12}$-μ-H$)L_3]^+$, where L is a tertiary phosphine or arsine, readily react with L, a process involving the dissociation of the Ru...H—C and Ru—C_8H_{12} bonds and the formation of the $RuHL_5^+$ cations.[44] The complexes (XIV) and (XVII) (Scheme 4) readily enter into a reaction with CO in which the Mn...H—C bond is dissociated, and



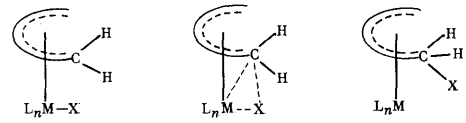
are converted into the complexes (η^3-allyl)$Mn(CO)_4$.[35,59] Compounds (XIV) and (XVII) are readily deprotonated on treatment with KH with evolution of H_2 and the formation of the anions (XXII) and (XXIII). When these are alkylated with MeI, the methyl group adds to the diene ligands and not to the Mn atom:[35,59]



(XXII) (XXIII)

The problems of the theoretical analysis of the structure and reactivity of CHB have attracted much attention. Several quantum-mechanical calculations have been made for the CHB both by the extended Hückel method (EHM) and by non-empirical methods. The characteristic features of the structure and of the unusual geometry of the alkylidene ligands in tantalum complexes and the characteristics of the activation of the C–H bond and of the hydrogen α-elimination reactions have been analysed.[170] In other studies by Hoffmann, the quantum-mechanical description of the activation of the C–H and H–H bonds by complexes having the d^n ($n > 0$) and d^0 configurations and also on the surface of the metal has been examined.[171,172] Calculations by the EHM have been performed for the model complexes $MeTiH_3$ and $Me_2TiH_5^{2-}$ and the influence of various factors and of the character of the ligands on the stabilisation of the 2e,3c-interaction in the methyl complexes has been discussed.[173] The electronic structures of the complexes $[Fe(\eta^3\text{-}C_8H_{12}\text{-}\mu\text{-}H)(CO)_3]^+$, $[Fe(\eta\text{-}C_8H_{12}\text{-}\mu\text{-}H)(PH_3)_3]^+$, $[Fe(C_6H_8\text{-}\mu\text{-}H)(CO)_3]^+$, $Mn(\eta\text{-}C_6H_8\text{-}\mu\text{-}H)(CO)_3$, and $Cr(\eta\text{-}C_8H_{10}\text{-}\mu\text{-}H)(PF_3)_3$ have been calculated[174] on the basis of the geometry obtained from XRD data.[35,41,63] The energy profile of the conversion of $[CpCo(PH_3)C_2H_5]^+$ into $[CpCo(PH_3)(C_2H_4)H]^+$ has been calculated and it has been concluded that the intermediate with the Co...H–C 2e,3c-bond is more stable than the ethylenemetal hydride complex.[175] *Ab initio* calculations have led to the optimisation of the geometry of the model complexes $Pd(Et)(H)(PH_3)$ and $Pd(H)_2(C_2H_4)(PH_3)$ and of the transition state between them, involving Pd...H–C 2e,3c-bonding, as well as the complexes $Pd(CH_3CHF_2)(H)(BH_3)$ and $Ni(Et)(H)(PH_3)$, and the role of the three-centre interactions in α-elimination reactions has been considered.[176] Optimisation of the geometry of the complex $Ti(Et)(PH_3)_2(Cl_2)(H)$(*ab initio* calculation) yielded a Ti–H distance of 2.23 Å and a Ti–C_α–C_β angle of 89°,[177] which agrees well with XRD data for Ti(Et)(Dmpe)Cl_3 (2.29 Å and 86° [75]). The most convenient structure of the complexes $Ti(Me)(PH_3)_2(X)_2(Y)$, which yielded a Ti–H distance of 2.51 Å and a Ti–C–H angle of 100° for X = Y = Cl,[178] which agrees well with experiment for Ti(Me)(Dmpe)Cl_3 (2.45 Å and 99° [75]), was calculated analogously. Calculations by the EHM have been performed for complexes containing molyb-denum[30] and cobalt.[52]

The survey of the structures and properties of CHB shows that a large number of complexes (B) (X = H) with M...H–C 2e,3c-bonds have already been obtained and characterised both in the crystal (more than 60 structures) and in solutions. The complexes are thermodynamically more stable than the corresponding alkene-, diene-, or polyenyl-metal hydride complexes (A) (X = H). The equilibrium (A) ⇄ (B) ⇄ (C), leading to the migration of hydrogen between the metal atom and the ligand, exists in solutions:



(A) (B) (C)

It has been suggested that there is an analogy between the complexes (B, X = H) and (B, X = alkyl) as regards structure, properties, and the dynamics of the migration of the group X and that in the complexes (B,X = alkyl) there is a possibility of the ready migration of the alkyl (Me, Et) group from the metal to the ligand.[51] A mechanism has been adopted for the polymerisation of olefins in the presence of Ziegler-Natta catalysts in which the key stage involves the migration of the alkyl group (R) from the metal atom to the olefin ligand and chain propagation via the insertion of R in the C–H bonds.[179] If such migration is possible in the complexes (B, X = alkyl), then they may be expected to manifest catalytic properties. It has been shown that the complexes $[(\eta\text{-}C_5Me_5)Co(L).(CH_2CHR\text{-}\mu\text{-}H)]^+$ do indeed catalyse the polymerisation of ethylene under mild conditions.[51]

In connection with the vigorous investigation of the activation of C–H and C–C bonds in alkanes,[10,11] new data have been obtained recently on the mechanisms of the reactions involving the oxidative addition (OA) of C–H bonds in the alkanes RH to low-valence rhodium, iridium, and rhenium complexes with formation of $R-(ML_n)-H$.[182–184] In the reactions of RH with rhodium compounds, intermediates of the type of CHB with the η^2-coordination of a C–H bond are apparently formed initially and then rapidly undergo intramolecular isomerisation to hydridoalkyl complexes.[184] A three-centre transition state with participation of M, C, and H atoms, preceding the dissociation of the C–H bond, has been proposed for the OA reactions.[185] The trajectories of the interaction of the M, C, and H nuclei in the course of the reactions have also been analysed:[60]

$$M + C\text{—}H \rightarrow C\text{—}(M)\text{—}H.$$

The data considered in the present review permit the conclusion that stable CHB with three-centre M...H–C bonds are apparently good models of the transition states in the OA reactions of alkanes.

It is important to emphasise that CHB can serve as intermediates in the various reactions of organometallic complexes with participation of acids. The H/D exchange reactions involving aromatic η-ligands in ferrocene, i.e. $(\eta\text{-}C_5H_5)M(CO)_{3-n}(P)_n$ [M = Mn or Re; (P) = phosphine; $n = 0-2$] and $(\eta\text{-}C_6H_6)Cr(CO)_2(L)$ (L = CO or phosphines), were studied in detail in 1962–1973 (see the relevant reviews[180,181]). A mechanism with protonation of the metal and the migration of an H atom to the η-ligand has been proposed for these reactions.[181] It is known that the complex $(\eta\text{-}C_4H_4)Fe(CO)_3$ (XXIV) is readily protonated[24] and rapidly exchanges H or D with CF_3COOD.[186] It has been concluded[24] that the Fe atom is protonated, but it is clear on the basis of the set of ^1H and ^{13}C NMR data, presented above in Section V, that the form of these spectra for the protonated form (XXIV) [the chemical shifts δ and the constants $J(^{13}C-H)$] agrees only with the formation of a three-centre Fe...H–C bond and an agostic H atom. The insertion of deuterium in η-ligands on protonation of the complexes (η-Dien)$Fe(P)_3$

by deuterioacids has already been mentioned above;[41] for -Dien = $\eta^4C_8H_{12}$, the CHB formed, with an Fe...H−C bond, was isolated and its structure was demonstrated by a structural method.[100,101] On the basis of the foregoing, it is logical to assume that the H/D exchange between the cyclic ferrocene ligands and the η-complexes of manganese, rhenium, and chromium, on the one hand, and acids, on the other, may also proceed via intermediates with bridging hydrogen.

During the preparation of the manuscript for the press, the following communications, describing the synthesis of complexes with agostic hydrogen atoms or postulating their formation as intermediates, were published. A review[187] deals with the activation of C−H bonds in alkanes by complex hydrides and organometallic compounds and the reactions and transformations of alkanes in the coordination sphere of the metal. The structure of $TiMeCl_3$ in the gas phase has been established by electron diffraction.[188] The following complexes with M...H−C bonds have been characterised by the XRD method; $Ru(SC_6H_2$-2,4,6-isoPr$_3)_4$ [189] and the cyclopalladised complexes $C_6H_4CHMe-NMe(Pr\text{-}iso)-Pd(L, L')$, where L, L′ = $(PPh_3)Cl$[190] or the acetylacetonato-group.[191] The agostic Fe...H−B bond in the complex $(PMe_3)_2(CO)FeCH(SR)S-BH_3$ has been detected by XRD.[192] Several polypyrazolylborate complexes with M...H−B bonds, including $[(Pir\ ¶)_2BH\text{-}\mu\text{-}H]Zr(Cp)Cl_2$,[193] $[(3,5\text{-}Me_2Pir)BH\text{-}\mu\text{-}H]Ru(\eta^4\text{-}C_8H_{12})H$,[194] and the complex $[(Pir)_2BH\text{-}\mu\text{-}H]_3Y$ containing three agostic Y...H−B bonds simultaneously have been characterised structurally.

In the studies quoted below, the conclusion that agostic hydrogen atoms are present was reached from ^1H and ^{13}C NMR spectra. The formation of the Li...H−C and Y...H−C bonds has been postulated for the complexes $Me_3CSC_6H_4Li(THF)_2$ [196] and $(C_5Me_5)_2YCH_2C_6H_3Me_2$.[197] The protonation of anionic ($n = -1$) or neutral ($n = 0$) η^4-diene complexes with acyclic and cyclic dienes of the type $[(\eta^4\text{-Dien})ML_x]^n$ leads to the formation of neutral or cationic η^3-allyl complexes with agostic hydrogen: $[(\eta^3\text{-allyl-}\mu\text{-H})\text{-}ML_x]^{n+1}$. The anionic complexes of manganese[198] and the neutral complexes of iron,[199,200] cobalt, rhodium, and iridium[201] (preliminary communication—see Buchmann and Salzer[54]) are protonated in this way. The Ru...H−C agostic bonds have been discovered in the complexes $[Ru(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_8H_{11}\text{-}\mu H)]^+$ [202] and $Ru(\eta^3\text{-}C_7H_{11}\text{-}\mu\text{-}H)(PPh_3)_2Cl$.[203] The synthesis and reactions of cationic dinuclear derivatives of biscyclopentadienylruthenium, where one of the hydrogen atoms of the bridging CH_3 group is coordinated to ruthenium, have been described.[204,205] The substitution of the agostic hydrogen atom in the dinuclear complex containing molybdenum and manganese by the isolobal fragment $Au(PMe_2Ph)$ has been carried out.[206] It was suggested that the reaction involving the dehydrogenation of alkanes to alkenes in the presence of $IrH_2(O_2.CCF_3)[P(C_6H_4F)_3]_2$ results in the formation of the catalytically active intermediate withan Ir...H−C bond.[207] The pathways leading to the redistribution of hydrogen in the protonated form of the complex $Mo(C_2H_4)_2$(*cis*-$Ph_2PCH=CHPPh_2)_2$ have been discussed[208] and it has been suggested that this process does not necessarily proceed via a 16-electron σ-ethyl intermediate.

The formation of agostic bonds in clusters has been observed in a number of studies. In the aryne complex $H_2Os_3(CO)_9(\mu^2\text{:}\mu^4\text{-}C_6H_4)$, there is rapid proton exchange between the ring and the metal, apparently via an intermediate with agostic hydrogen;[209] analogous intermediates have been proposed for the hydrogen substitution and elimination reactions in $Fe_3(CO)_9(\mu\text{-}H)_3(\mu\text{-}CCH_3)$.[210] It has been shown by ^1H and ^{13}C NMR that the protonation of the heterometallic anionic carbido-clusters $MFe_3(CO)_{13}C^{2-}$ (M = Cr or W), $MnFe_3(CO)_{13}C^-$, and $RhFe_3(CO)_{12}C$ with the "butterfly" skeleton leads to the formation of agostic Fe...H−C bonds between the hydrogen of the methylidyne fragment and the iron atom.[211]

The interaction of CH_4 and CD_4 with organometallic complexes has been investigated by IR spectroscopy in matrices at 12−16 K. The formation of the relatively unstable compounds of the type $L_nM...H-CH_3$ has been postulated for Cp_2Ni, $(C_5Me_5)_2Ni$, $(C_5Me_5)_2Mn$, and (arene)$M(CO)_3$.[212] The quantum-chemical aspects of the electronic structure, the problem of the relative stabilities of the intermediate systems with M−H and M−C bonds, the coordination of methane, and the interaction of C−H bonds with the metal complex centre have been examined in a monograph[213] and in the literature quoted therein. The results of theoretical calculations of the electronic structure, stability, and reactivity of complexes with M...H−C,[214-218] Fe...H−E (E = B or C),[219] and Ti−Si−C[220] bonds have been described in a number of communications. Quantum-chemical calculations for compounds with Mn−H−Si bonds have been carried out.[221] Evidently both the experimental and the theoretical chemistry of complexes with agostic hydrogen atoms continues to develop very vigorously.

¶Pir = pyrazolyl (Translator).

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Dibenzylideneacetone Complexes of Transition Metals

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Information on dibenzylideneacetone complexes of transition metals is reviewed. Their methods of preparation, physicochemical and chemical properties, and also applications as reagents and catalysts are discussed. The bibliography includes 162 references.

CONTENTS

I.	Introduction	1194
II.	Dibenzylideneacetone as a ligand	1194
III.	The structures of DBA complexes of transition metals	1196
IV.	Methods of preparing DBA complexes of transition metals	1198
V.	Chemical properties of DBA complexes of transition metals	1200
VI.	Use of DBA complexes of the platinum metals as homogeneous catalysts	1204

I. INTRODUCTION

Immediately after they were first prepared,[1,2] transition metal complexes with dibenzylideneacetone (DBA) (palladium and platinum complexes in the first place) attracted the attention of both organometallic chemists and synthetic chemists because of their high reactivity and ease of preparation, and the debate concerning their structure continued until 1974 when the structure was reliably established by X-ray structure analysis. DBA complexes of palladium and platinum are now firmly established in the armoury of chemists as convenient starting materials for the preparation of organic derivatives of these metals that are difficult to obtain by other methods, and also as homogeneous catalysts in a great variety of reactions (allylation, nucleophilic addition reactions, alkylation, cross-linking, etc.).

The aim of this review was to survey the available material on the preparation of DBA complexes, especially those of the platinum metals, to show how the formation of complexes with a specific structure (monomeric DBA derivatives, dimeric complexes, solvates of dimers) depends on the preparation conditions used and the reagents, to outline the synthetic possibilities of this class of compound, which is highly reactive, and to summarise the very disjoint information on the use of DBA complexes of palladium and platinum as catalysts. However before doing this it is necessary to discuss the properties of free dibenzylideneacetone which characterise it as a potential ligand.

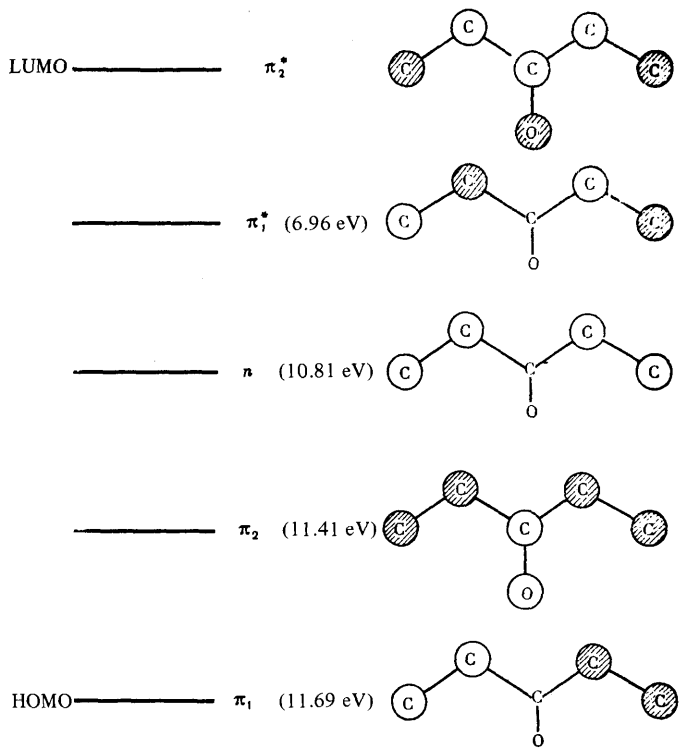


Figure 1. Frontier molecular orbitals of divinyl ketone.

II. DIBENZYLIDENEACETONE AS A LIGAND

To assess DBA as a ligand in complexes with transition metals it is necessary to be aware of its conformational properties and electronic structure because these are controlling factors in coordination. To assess the second factor it is sufficient to have data on the nature of the frontier orbitals, i.e. the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the DBA molecule. Such an assessment has been made;[3] the simplest analogue of DBA, divinyl ketone $CH_2=CHCOCH=CH_2$ in the *s-cis,s-cis* conformation, was considered as the model molecule. The energies of the frontier orbitals of the divinyl ketone molecule[3] are shown in Fig.1.

Analogous data for acrolein $CH_2=CHCHO$ [3] and ethylene† are given in Fig.2 for comparison. The HOMO of divinyl ketone is an oxygen p_y-orbital which is a non-bonding AO of the oxygen in the

†The energy of the HOMO of ethylene was taken to be the ionisation energy I = 10.62 eV;[4] the energy of the LUMO was calculated from u.v. spectroscopic data (the energy of the $\pi \rightarrow \pi^*$ transition is 61 000 cm^{-1}).[5]

carbonyl group (the charge on the oxygen, $q_O = 0.82$, agrees well with results obtained by other authors[6]). Its energy (10.81 eV) is similar to the energy of the corresponding MO in acrolein (10.15 eV) but these orbitals have different symmetries; in the acrolein molecule the non-bonding AO of the oxygen in the carbonyl group is oriented along the x axis, i.e. it is a p_x-orbital.

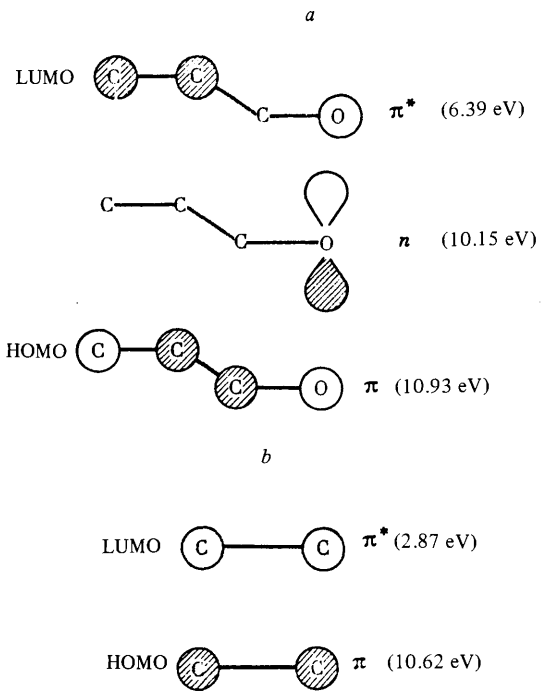


Figure 2. Frontiers molecular orbitals of: *a*) acrolein; *b*) ethylene.

The next occupied MO in the divinyl ketone molecule (and also in acrolein) is the π-bonding MO of the C=C bond with an energy of 11.69 eV (11.76 eV in acrolein); the corresponding antibonding π*-MO's have energies of 6.96 eV for divinyl ketone and 6.39 eV for acrolein. For ethylene the energy of the π-MO is 10.62 eV which is comparable with the energies of the corresponding MO's in divinyl ketone and acrolein; the energy of the lowest π*-MO in ethylene is 2.87 eV which is considerably different from the energy of the corresponding orbitals in divinyl ketone. Hence the formation of a $d \rightarrow \pi^*$ type metal–ligand donor-acceptor back bond, particularly with metals in low oxidation states for which the highest occupied d orbitals have energies in the region of 8 eV,[7] will be energetically more favourable for the two α,β-unsaturated carbnonyl compounds (acrolein and divinyl ketone) than for ethylene. This conclusion agrees with results[8] indicating an increase in the stability of olefinic π-complexes of transition metals in low oxidation state when acceptor substituents are introduced into the olefin molecule.

The most suitable donor orbitals in the divinyl ketone molecule are the n- and π-orbitals and the second are more favourable although their energy is somewhat lower ($\Delta E = 0.9$ eV). As a rule, therefore, in α,β-unsaturated carbonyl compounds the double bond is much more easily coordinated than the carbonyl group. Nevertheless, bidentate coordination, with the α,β-unsaturated ketone forming chelate or bridging complexes, is also possible.[3,8] Hence, *a priori*, for DBA the possibility of both $n \rightarrow d$‡ and $\pi \rightarrow d$ types of coordination cannot be excluded. As will be shown below, both occur.

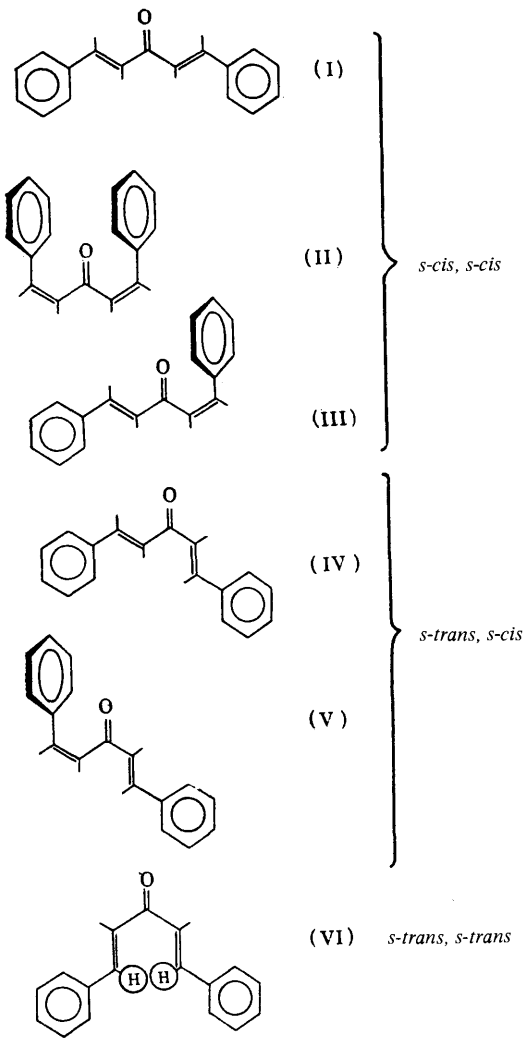


Figure 3. Possible conformations of DBA.

We shall now discuss the conformational properties of DBA. In principle it is possible to have the following alternatives of a planar arrangement of the C=C and C=O bonds relative to each other combined with different configurations of the ethylenic bonds (Fig.3):[9,10] three *s-cis,s-cis* conformations (I, II, and III), two

‡ $n \rightarrow d$-Coordination was assumed for DBA in its complexes with Pd^0 and Pt^0;[2] see also Ref. 3.

s-trans,s-cis (IV and V), and one *s-trans,s-trans* conformation (VI). However, Stuart–Brigleb models and van der Waals diagrams with Stuart–Brigleb radii show that the planar *s-trans,s-trans* structure (VI) is impossible owing to repulsion between the β and β′ hydrogen atoms (the overlap is 1.2 Å); structures I and IV§ are completely planar and hence energetically more favourable [the small overlap (0.21 Å) between the α and β′ hydrogen atoms in structure IV can be disregarded].[12] In structures II, III, and V steric hindrance forces one or both of the phenyl groups out of the plane of the double bonds. U.v.,[12,13] n.m.r.,[14] and i.r. [9] spectroscopic data also indicate that DBA molecules occur in solution only with a *trans* configuration of the two ethylenic bonds. This is also supported by dipole moment data.[14] Thus the conformational characteristics of DBA in solution define it as an olefin in which the two double bonds are unlikely to be coordinated to the same metal atom because they have different symmetries. Coordination of DBA as a 1,4-diene is therefore less favoured and effectively two possibilities remain: DBA acts as a bridging ligand in binuclear complexes or is an ordinary unidentate olefin with somewhat greater potentialities for donor-acceptor back bonding compared to ethylene. How such potentialities are realised will be shown below.

Table 1. U.v. spectra (λ in nm) of DBA, TBAA, and their palladium and platinum complexes.[16,17]

DBA	TBAA	$Pd(DBA)_2$	$Pt(DBA)_2$	$Pd_2(DBA)_3.CHCl_3$	$Pd_3(TBAA)_3.CHCl_3$	Assignment
233 m.	231 m.	235 m.	235 m.	236 m.	234 m.	π→π*
325 s.	320 s.	336 s.	336 s.	300 sh. 321 s.	320 s.	n→π*
374	—	378	—	—	—	unassigned
520 w.	—	538 m.	568 m.	—	—	d→d

Note. s. = strong, m. = medium, w. = weak, sh. = shoulder.

Table 2. I.r. spectra (cm^{-1}) of DBA, TBAA, and their palladium and platinum complexes.[16,17]

DBA	TBAA	Pd $(DBA)_2$	Pt $(DBA)_2$	$Pd_2(DBA)_3.CHCl_3$	$Pd_2[(C_6D_5CH=CH)_2CO]_3.CHCl_3$	$Pd_3(TBAA)_3.CHCl_3$	Assignment
1667 m.sh.	1667 m.sh.	—	—	—	—	—	—
1651 s.	1650 s.	1656	1652	—	—	—	ν(C=O)
1627 m.	1628 m.	1613	1624	1620, 1614 s.	1620, 1615 s.	1620, 1614 s.	$\nu(C=C)_{aliph}$
1591 s.	1591 s.sh.	—	1593	1600 s.	1591 m.	1590 m.	$\nu(C=C)_{arom}$
1574 s.	1575 s.	1579	1579	1574 m.	1550 m.	1575 m.	—
—	—	1544	1527	—	—	—	—
983 s.	981 s.	—	—	975 w.	977 w.	981 w.	$\sigma(CH)_{trans}$

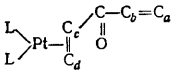
III. THE STRUCTURES OF DBA COMPLEXES OF TRANSITION METALS

As indicated above, in its metal complexes DBA can act as both an *n*- and a π-donor ligand but in the latter case, owing to its conformational characteristics, DBA is less likely to form diene complexes of the chelate type and more likely to act as a uni- or bi-dentate π-olefinic ligand.

The available X-ray structural data indicate that all the possible modes of bonding between DBA and transition metals occur.

However, we shall first discuss the spectroscopic (u.v., i.r., and n.m.r.) properties of DBA complexes.

Table 3. Parameters of the ^{13}C n.m.r. spectra of DBA and $L_2Pt(DBA)$ complexes.[21]



L	C_a	C_b	C_c	C_d	$J(Pt-C_c)$	$J(Pt-C_d)$
PEt_3	124 6	134.8	49.7	61.0	235	180
$AsEt_3$	123.0	135.8	46.3	58.0	275	185
DBA (uncoord.)	135.4	142.7	135.4	142.7	—	—

The u.v. spectra of uncoordinated DBA, the complexes $Pd(DBA)_2$, $Pt(DBA)_2$, and $Pd_2(DBA)_3.CHCl_3$, and also tribenzylideneacetylacetone (TBAA) and $Pd_3(TBAA)_3.CHCl_3$ are compared in Table 1.

It is clear that the bands due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in DBA show no change in either position or intensity on coordination. In the opinion of the authors of Refs.16 and 17 this indicates that the carbonyl group in DBA is not involved in the coordination.

I.r. spectroscopic data for DBA, $Pd(DBA)_2$, $Pt(DBA)_2$, $Pd_2(DBA)_3.CHCl_3$, $Pd_2[(C_6D_5CH=CH)_2CO]_3.CHCl_3$, TBAA, and $Pd_3(TBAA)_3.CHCl_3$ are compared in Table 2.

The conclusions drawn from the i.r. spectra by different authors are very contradictory. The data in Table 3 [Table 2? (Ed. of Translation)] can provide support for coordination both via the carbonyl group and via the C=C double bonds in DBA.

Next we shall consider the n.m.r. spectroscopic data for DBA and its complexes. The similarity between the ^1H n.m.r. spectral characteristics of uncoordinated DBA and complexes of the type $M(DBA)_2$ (M = Pd, Pt) was noted as far back as 1971.[2] In compounds of the type $M_2(DBA)_3$ (M = Pd, Pt) the signals of the olefinic protons in DBA are shifted to low field on coordination with the metal atom.[18,19] ^1H n.m.r. spectroscopic data indicate that only one of the two C=C bonds in DBA is coordinated to the platinum in $L_2Pt(DBA)$ type complexes.[20] This was also confirmed for the complexes $L_2Pd(DBA)$ (L = PPh_3, PEt_3, PPh_2Me, $AsPh_2$, $AsEt_3$) by ^{13}C n.m.r. spectrosocpy (Table 3).[21]

N.m.r. spectroscopic data thus show that the coordination of the DBA is of the $\pi \rightarrow d$ type and the DBA complexes of Pd and Pt can be regarded as π-olefin derivatives of these metals.

The question of the structure of DBA compounds of palladium, platinum, and rhodium was finally resolved by X-ray structure analysis.

Dibenzylideneacetone forms several types of complex: $M(DBA)_2$ (M = Pd, Pt), $M(DBA)_3$ (M = Pd, Pt), $M_2(DBA)_3.Solv$ (M = Pd, Pt), $MO_2Cl_2(DBA)_2$ (M = U), and $C_5Me_5M(DBA)$ (M = Rh). X-Ray structure determinations have been carried out on all these types except $M(DBA)_2$.

§However, measurements of the molar Kerr constants of DBA can be reconciled with an *s-cis,s-cis* conformation only on condition that the phenyl groups are rotated by 26.5° around the 1,4-axes.

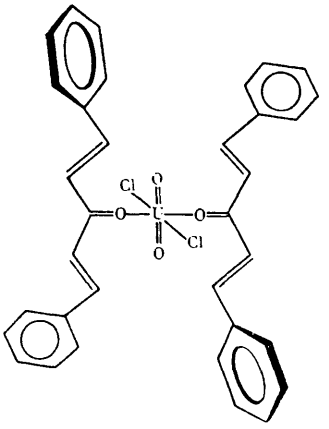


Figure 4. Structure of $UO_2Cl_2(DBA)_2$ in the crystal.

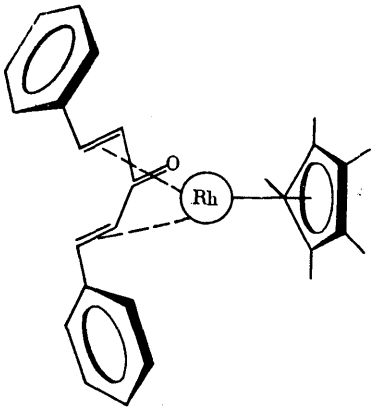


Figure 5. Structure of $C_5Me_5Rh(DBA)$ in the crystal.

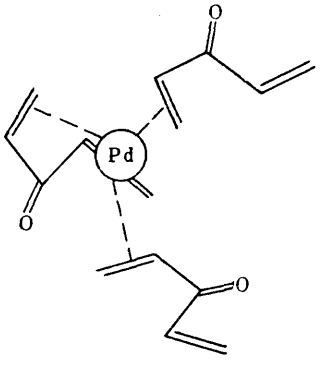


Figure 6. Structure of $Pd(DBA)_3$ in the crystal.

In the uranyl compounds the DBA is coordinated to the uranium atom via the oxygen atom of the carbonyl group (Fig.4);[22-24] the ligand is in the *s-cis,s-cis* conformation and the changes in the C=O and CH=CH bond lengths in DBA owing to coordination are unimportant. The phenyl rings are in the plane formed by the

$$-CH=CH-\overset{\overset{O}{\|}}{C}-CH=CH-,$$

system, i.e. the DBA is in the planar *cis,cis*-form (I) which is energetically the most favourable for uncoordinated DBA.

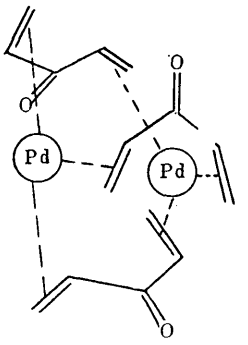


Figure 7. Structure of $Pd_2(DBA)_3.CH_2Cl_2$ in the crystal.

In the rhodium complex (Fig.5) DBA acts as an η^4-dienone ligand.[25,26] The coordinated DBA has the symmetrical *s-trans,s-trans* configuration (VI) which, as has already been mentioned, is impossible for the uncoordinated ligand because of the intramolecular H...H interaction between C(3)H and C(5)H; this distance is 1.2 Å in free DBA and 1.89 Å in the rhodium complex. The DBA molecule in this complex is under considerable strain and this is evidently the reason for the high catalytic activity of $C_5Me_5Rh(DBA)$. Tris(dibenzylideneacetone)palladium (Fig.6) is a tris-olefin complex of Pd^0.[27] Each of the three pentadiene ligands is coordinated by only one C=C bond, the DBA molecule is in the most favourable *s-cis,s-trans* conformation (IV), and the relatively small changes in the DBA bond lengths on coordination reflect the weakness of the metal–ligand bond in these complexes.

In the solvated complexes $Pd_2(DBA)_3.Solv$ the three ligands are bonded to the palladium atoms in different ways depending on the nature of the solvent Solv.[28,29] When Solv = CH_2Cl_2 two of the DBA molecules are in the *s-cis,s-trans* conformation but the third is in the *s-cis,s-cis* form (Fig.7). When Solv = $CHCl_3$ all three DBA ligands are in the *s-cis,s-trans* conformation. The factors determining the conformational properties of the DBA ligands in the $Pd_2(DBA)_3$ complexes are considered[28,29] to include not only the intramolecular contacts in DBA itself but also interligand interactions and, all in all, they will lead to an optimally strong π-bond between the metal and the olefin fragment of the DBA. On these grounds the most favourable DBA conformation will be *s-cis,s-cis*, in which the two C=C fragments are oriented approximately in the trigonal planes of the two Pd atoms. However, this does not provide sufficient separation between the two metal centres. The *s-cis,s-trans* conformation is more suitable from the latter point of view.

The interaction-between-the-metal-atoms factor does not of course apply in "monometallic" complexes but the *s-cis,s-trans* conformation usually still occurs because of the DBA–DBA interligand interactions. However, in (bipy)Pd(DBA), where there are no such interactions, the DBA ligand is in the *s-cis,s-cis* conformation (W-conformation) (Fig.8).[30]

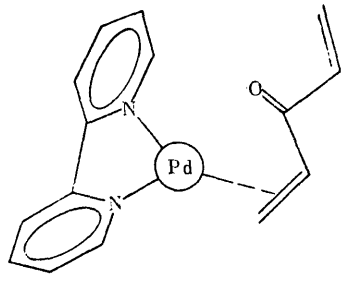


Figure 8. Structure of (bipy)Pd(DBA) in the crystal.

The available experimental data on the strutures of DBA complexes in the crystalline state thus agree fairly well with the preliminary assessments discussed above. The structures of the complexes in solution have been studied by n.m.r. spectroscopy.[31-33]

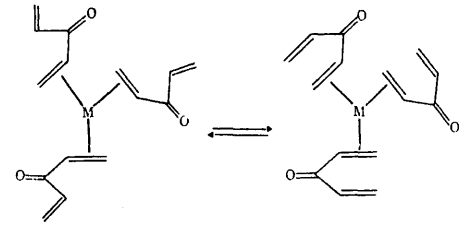
In a $CDCl_3$ solution the $Pd_2(DBA)_3.CHCl_3$ molecule has the three DBA ligands in the *s-cis,s-trans* conformation,[33] as in the crystal. Similarly, the ^1H n.m.r. spectrum of $Pd_2(DBA)_3.CH_2Cl_2$ in CD_2Cl_2 shows that one of the DBA ligands is in the *s-cis,s-cis* form, also agreeing with the X-ray structural results.[29]

There was found to be a linear correlation between the values of J(AB) and δ(H) for the olefinic protons in the DBA ligands. Hence the spin–spin interaction is determined by the same factors as the chemical shift. In the opinion of Kawazura et al.[31] the ability of the ligand to form a donor-acceptor back bond with the metal (π-back-donation) is one such factor. The capability of olefin ligands for back donation in turn depends on two factors: the geometry of the olefin (*cis* or *trans*) and the distance between the metal atoms and the double bond.

From the results of MO calculations for olefinic complexes of nickel[34] with the metal and the C=C bond located in the same plane, *trans*-olefins are more capable of back donation than *cis*-olefins. In the case where all three DBA ligands are in the *s-cis,s-trans* form (the $CHCl_3$ solvate) the mean distances between the Pd and the C=C bond (2.19–2.22 Å) are shorter than in the CH_2Cl_2 solvate where one ligand is in the *s,cis,s-cis* conformation. The interaction of these two trends evidently also determines the structure of the complexes in solution.

For the analogous platinum complex $Pt_2(DBA)_3.CHCl_3$, whose structure has not been determined by X-ray diffraction, ^1H n.m.r. data for a solution in $CDCl_3$ [32] indicate that two of the DBA ligands have the *s-cis,s-trans* conformation and one is in the *s-cis,s-cis* form, as in Ref.31; the connection between J(Pt–H) and the capability of DBA for back donation is discussed.

Studies have been made of the ^1H n.m.r. spectra of $M(DBA)_3$ complexes (M = Pd, Pt) [23] which will be more dynamic in solution as compared to the binuclear $M_2(DBA)_3$ compounds.[27] In $CDCl_3$ at –60 °C all three coordinated DBA ligands have an *s-cis,s-trans* conformation with the *s-trans* fragment of the ligand bonded to the metal atom. On raising the temperature the following equilibrium occurs:



In the Pt complex the amount of the equilibrium form containing the *s-trans,s-trans* ligand may be fairly large. The authors attribute this to more effective back donation in the Pt derivative than in the Pd complex.

Thus DBA complexes of Pd and Pt have the same structure in the crystalline state and in solution. The conformational and energy characteristics of DBA as a potential ligand which were discussed above apply almost totally in its complexes with the platinum metals. In these derivatives DBA acts as an olefin with an electron-accepting substituent and the compounds discussed can be regarded as π-olefin complexes of platinum metals in low oxidation states.[35]

IV. METHODS OF PREPARING DBA COMPLEXES OF TRANSITION METALS

For the preparation of DBA complexes of transition metals only one method, the reaction of an excess of DBA with a metal salt in the presence of a base, is used.[1,2,16,18,21,28,35-39] The reactions are usually carried out in an alcoholic or aqueous-alcoholic solution, with sodium acetate or carbonate as the base.

A second method, the substitution of other ligands by DBA,[39] has no preparative value and is used only to determine the comparative stability of the complexes of palladium with DBA and TBAA.¶

$Pd(DBA)_2$ was first obtained[1] by adding sodium acetate to a methanol solution of a mixture of Na_2PdCl_4 and DBA (DBA/Pd $\geqslant$ 3) heated to 60 °C. Cooling to room temperature gave a brownish black crystalline complex of composition $Pd(DBA)_2$ which is fairly stable in air in the solid state but slowly decomposes in solution depositing palladium metal. This complex is sparingly soluble in CH_2Cl_2, $CHCl_3$, and benzene forming highly coloured solutions.

$Pd(DBA)_2$ was later obtained[37] by adding a hot aqueous solution of K_2PdCl_4 to an alcoholic solution of a three-fold excess of DBA and an eight-fold excess of NaOAc in alcohol in a nitrogen atmosphere. However, the products had different i.r. spectra, as was noted in Ref.28. If the complex obtained by the latter method[37] is recrystallised from $CHCl_3$ or CH_2Cl_2 the product has an i.r. spectrum similar to that of the specimen obtained by the first method.[1] A detailed investigation of the latter showed[18,21] that its recrystallisation from $CHCl_3$ or any other organic solvent gives complexes with the composition $Pd_2(DBA)_3.Solv$, where Solv represents a molecule of the solvent used. A very convenient method for preparing $Pd(DBA)_2$

¶TBAA, PhCH=CHCOC(COCH=CHPh)=CHPh, (m.p. 112 to 113 °C) has an *s-cis,s-trans* conformation according to i.r., u.v., and n.m.r. spectroscopic data.[39]

is the addition of palladium chloride to a hot (~50 °C) methanol solution of a mixture of DBA and AcONa (Pd/DBA/AcONa ratios = 6/20/50).[18] Ater the reaction mixture has been stirred at 40 °C for 4 h a reddish purple precipitate with m.p. 135 °C and the composition $Pd(DBA)_2$ is formed. This is evidently the complex the authors of Refs.1 and 2 were dealing with. Dissolving it in hot chloroform gives a dark violet solution from which purple acicular crystals with m.p. 122–124 °C and the composition $Pd_2(DBA)_3.CHCl_3$ are deposited when ether is added. If $Pd(DBA)_2$ is dissolved in benzene, toluene, or dichloromethane, the corresponding solvates $Pd_2(DBA)_3$.Solv, where Solv = C_6H_6, C_6H_5Me, or CH_2Cl_2, crystallise out.[28] It is interesting that the complexes formed by *p,p'*-dimethoxydibenzylideneacetone[18,21] and *p,p'*-di-isopropyldibenzylideneacetone[25] contain no solvent molecules but have the composition Pd_2L_3, where L is the corresponding DB derivative. Interconversion of the $Pd_2(DBA)_3$.Solv complexes occurs on recrystallisation from the appropriate solvent.[18] However, in the preparation of $Pd_2(DBA)_3$.Solv the use of chloroform is recommended[28] because recrystallisation from this solvent gives the maximum product yield (~80%). The palladium complex with *p,p'*-di-isopropyldibenzylideneacetone mentioned above was obtained by dissolving the PdL_2 initially formed in THF and then adding methanol. It is interesting that in the preparation of tris(di-isopropyldibenzylideneacetone)dipalladium[36] the reagents were mixed in the "reverse" order: anhydrous sodium acetate was added to a hot mixture of DBA and Na_2PdCl_4 in methanol; the yield of the final product was 75%.

TBAA reacts with $PdCl_2$ and AcONa under the conditions described above[18] to form, after recrystallisation from $CHCl_3$, the purple acicular complex $Pd_3(TBAA)_3.CHCl_3$ in an 84% yield.[39] As with DBA, the precipitate formed initially gives the corresponding solvate $Pd_3(TBAA)_3$.Solv on crystallisation from $CHCl_3$, CH_2Cl_2, or benzene. Unfortunately the composition of the initial precipitate was not determined. Like the $Pd_2(DBA)_3$.Solv complexes, the TBAA complexes can be interconverted on recrystallisation from the appropriate solvent.† When the reaction of $PdCl_2$ with TBAA is carried out in cyclohexanol instead of methanol, the cyclohexanol is oxidised to cyclohexanone in an 81% yield calculated on the basis of the palladium chloride used in the reaction.[39]

Another palladium complex with DBA, mononuclear tris(dibenzylideneacetone)palladium, is also known. $Pd(DBA)_3$ can be obtained in two ways: by adding a four-fold excess of DBA to a benzene solution of $Pd_2(DBA)_3.C_6H_6$ [38] or by the reaction of Na_2PdCl_4 with DBA in aqueous alcohol in the absence of sodium acetate.[37] In the first case a mixture of the complex $Pd(DBA)_3$ with free DBA is formed. Chemical analysis of the complex indicates the presence of one molecule of benzene to each molecule of the compound. $Pd(DBA)_3.C_6H_6$ dissociates readily in solution, giving $Pd(DBA)_2$. Thus, taking account of the results from Ref.28, we may conclude that there is a series of DBA complexes of palladium in equilibrium with each other:

$$Pd_2(DBA)_3 \overset{DBA}{\rightleftharpoons} Pd(DBA)_2 \overset{DBA}{\rightleftharpoons} Pd(DBA)_3.$$

A similar mononuclear tris(dibenzylideneacetone)platinum complex has been obtained.[2] It is prepared by boiling K_2PtCl_4 with a three-fold excess of DBA in methanol in the presence of sodium acetate. Air or oxygen must be present but its role is not clear; chemical anlaysis shows that the product contains no "extra" oxygen. Maitlis et al.[36] mention that $Pt(DBA)_2$ is formed by the reaction of K_2PtCl_4 with DBA in the absence of oxygen; however, in later work[37] these authors, referring to methods for preparing $Pt(DBA)_n$ (n = 2, 3), do not mention anything about the determining effect of oxygen or air. A comparison of methods for preparing $Pt(DBA)_2$ and $Pt(DBA)_3$ shows that the latter is formed in a more prolonged reaction (4 h as against 10 min) and at higher DBA/Pt and AcONa/Pt ratios (17/1.2 and 30/1.2 respectively, as against 10/3.6 and 35/3.6). Furthermore $Pt(DBA)_3$ is formed at 40 °C but $Pt(DBA)_2$ in boiling ethanol (~80 °C). The two complexes are very different in colour: $Pt(DBA)_2$ is purplish black and $Pt(DBA)_3$ is canary yellow. The tris-complex dissociates completely to $Pt(DBA)_2$ and free DBA when dissolved in organic solvents;[2] this is indicated by cryoscopic determinations of the molecular weight in benzene. $Pt(DBA)_2$ forms the solvates $Pt_2(DBA)_3$.Solv when it is dissolved in such solvents as C_6H_6, $CHCl_3$, toluene, etc.[19] These results have been confirmed for the platinum complex with *p,p'*-di-isopropyldibenzylideneacetone.[36] The addition of an aqueous solution of K_2PtCl_4 to a boiling solution of NaOAc and *p,p'*-di-isopropyldibenzylideneacetone in ethanol (K_2PtCl_4/NaOAc/di-isopropyl-DBA ratios = 7.2/73.0/15.7) followed by boiling for 1 h gave a black complex of composition PtL_2, where L = *p,p'*-di-isopropyldibenzylideneacetone, which in THF forms a dark purple solution. After evaporation of the solution and the addition of methanol violet-black crystals of composition Pt_2L_3 slowly crystallised out. The complex obtained in Ref.16 is evidently the solvate $Pt_2(DBA)_3.CH_2Cl_2$ and not $Pt(DBA)_2$,[19] because it was produced by crystallising the crude $Pt(DBA)_2$ from dichloromethane. In the same work[16] the mixed complexes $L_2Pt(DBA)$ (L = PPh_3) were obtained by the reaction of L_4Pt with DBA in toluene; this is another example of the preparation of DBA complexes by ligand substitution. Triphenylphosphine is easily displaced from $Pt(PPh_3)_4$ by other α,β-unsaturated olefins;[16] the complexes $(Ph_3P)_2PtL'$, where L' is 4-phenylbut-3-en-2-one or 1,3-diphenylprop-2-en-1-one, were obtained in this way. The spectroscopic properties of these complexes are similar to those of the DBA complexes. It is interesting, in connection with this, that 4-phenylbut-3-en-2-one (benzylideneacetone) forms complexes with Fe^0 which have an η^2-olefinic or η^{1-4} heterodiene structure[17,40–47] depending on the nature of the other ligands bonded to the iron atom. The formation of η^2-olefinic complexes has also been observed in the reaction of 4-methyl-pent-3-en-2-one with the Pt^{II} derivatives K_2PtCl_4 and $(C_2H_4)_2Pt_2Cl_4$;[48,49] with Pd^{II} π-allylic complexes are formed.[50,51]

Thus the DBA complexes with palladium and platinum which were originally thought to have the composition $M(DBA)_2$ in fact have the more complex structure $M_2(DBA)_3$.Solv; another type of DBA complex, $M(DBA)_3$, is also known for palladium and platinum. Finally, there are reports of DBA complexes of rhodium[25] and uranium[22] containing respectively one and two molecules of the ligand per metal atom. The rhodium derivative $Me_5C_5Rh(DBA)$ was obtained[25] by the reaction of di-μ-chloro-bis(pentamethylcyclopentadienylrhodium) with DBA in alcohol in the presence of Na_2CO_3, i.e. by the usual method of preparing DBA complexes of transition metals. The uranium complex $UO_2Cl_2(DBA)_2$ was isolated in the photodimerisation of DBA in the presence of UO_2Cl_2.[22] It has long been known that DBA is dimerised to 1,3-diphenyl-2,4-dicinnamoylcyclobutane by UO_2Cl_2 [52] and $SnCl_4$ [53] whereas photodimerisation in the absence of metal salts gives 1,2-diphenyl-3,4-dicinnamoylcyclobutane.[54] The reaction of DBA with metal salts has also been mentioned elsewhere.[55–59] For

†Hence the scheme given in Ref.18 is also valid for TBAA complexes.

example, under the action of alkali metal alkoxides the semicarbazone of *trans,trans*-DBA cyclises to *cis*- and *trans*-1,2-diphenylcyclopent-3-enes.[55] Five-membered alicyclic compounds are formed by the reaction of DBA with Os^{IV} salts in the presence of Zn dust;[56] reductive dimerisation gives 1-styryl-2-cinnamoyl-3,4-diphenylcyclopentanol in a quantitative yield. Electrochemical reduction of DBA or the action of such reducing agents as Mg and Zn amalgams also lead to reductive dimerisation but the yield of the cyclopentanol mentioned above is very small.[57-59] Similar reductive dimerisation reactions occur in the $Os^{IV}-Zn$ system with other α,β-unsaturated ketones.[56]

V. CHEMICAL PROPERTIES OF DBA COMPLEXES OF TRANSITION METALS

Two types of reaction are characteristic for DBA complexes of transition metals: substitution of the ligands without changing the oxidation state of the central metal atom and oxidative addition which, as a rule, takes place with substituion of the DBA ligands. The reactivity of the palladium compounds has been studied most thoroughly because these compounds are readily available and stable. Note that the kinetic and thermodynamic stabilities of the DBA complexes of Pd and Pt are diametrically opposed. The DBA ligand is the most labile of the known π-ligands[60] because it is easily displaced even by such ligands as acetylenes; however, the thermodynamic stability of DBA complexes of transition metals is comparable with the stability of such strong complexes as the π-allylic complexes. For example, the dissociation energy of the Pt−DBA bond is 273 kJ mol^{-1} [61] which is greater than the corresponding energy of the Pd−π-allyl bond in bis-π-allylpalladium chloride (237 kJ mol^{-1}).

1. Ligand Substitution Reactions

Even in the earliest work on the chemistry of DBA complexes[1,2] the high tendency for coordinated DBA to be replaced by various ligands was noted. The strength of the reaction depends on the nature of the metal atom and the properties of the substituting ligand. A soft base such as triphenylphosphine reacts with tris(dibenzylideneacetone)dipalladium, replacing all the ligands and forming tetrakis(triphenylphosphine)palladium:[18,21] even a large excess of the harder base bipyridyl (bipy) replaces only two DBA molecules on reaction with $Pd_2(DBA)_3$ in acetone, forming the unstable complex (bipy)Pd(DBA).[18,21] Pyridine (py) and *o*-phenanthroline (phen) react similarly. Complete replacement of DBA from the platinum complex $Pt_2(DBA)_3$ occurs only on reaction with the stronger π-acceptor $AsPh_3$ (reagent ratio $AsPh_3$:$Pt_2(DBA)_3$ = 4);[18] reaction with an excess of R_3P (R = Me, Et, Ph) or a deficiency of $AsPh_3$ [$AsPh_3$: $Pt_2(DBA)_3$ = 2] gives the partially substituted products $L_2Pd(DBA)$ (L = PMe_3, PEt_3, PPh_3, $AsPh_3$).[16] These results indicate that the DBA complexes with platinum are more stable and also that the strength of the metal−DBA bond increases with the degree of substitution. This may be due to the stabilising effect of the *n*-donor ligands; however, the results of a thermogravimetric study[18,21] show that the stepwise detachment of DBA ligands from a palladium complex occurs even in the absence of other ligands.

From a practical point of view the reactions of DBA complexes with olefins are the most interesting because they are at present the only method for preparing olefinic π-complexes of Pd^0 of the type L_2Pd(olefin).[62]

(a) Reactions with olefins. $Pd_2(DBA)_3$ reacts with olefins without *n*-donor ligands being present but the olefinic complexes formed have not been isolated because they decompose to palladium metal and free DBA under the reaction conditions used (acetone, room temperature).[18,63,64] Stable (olefin)PdL_n complexes are formed if ligands such as bipy, phen, or $P(OR)_3$ are present in the reaction mixture together with the olefin.[18,63-65] The stability of the complexes formed is determined by both the nature of the olefin and the basicity of the ligand L. Only olefins with electron-accepting substituents form stable complexes; for stable complexes to be formed the lower the π-accepting ability of the olefin the greater must be the σ-donor properties of the ligands. A table showing the effect of the nature of the olefin and the ligand L on the stability of (olefin)PdL_n type complexes has been published.[18,64]

Table 4. Stability of the palladium olefin π-complexes (olefin)PdL_n.[66]

Olefin	*e*	L					
		bipy	phen	tmeda *	$P(OPh)_3$	$P(OMe)_3$	PPh_3
Maleic anhydride	2.25	++	++	++	++	++	–
Dimethyl fumarate	1.49	++	++	++	++	++	–
Divinylsulphone	1.33	++	+	+	+	+	–
Dimethyl maleate	1.27	++	++	+	–	–	–
Acrylonitrile	1.20	++	++	–	–	–	–

Note. ++) complex stable and can be isolated; +) a complex is formed but decomposes during isolation; –) no complex formed.

*tmeda = tetramethylethylenediamine.

The *e* values given in Table 4 are taken from Ref.66; they characterise the electronic properties of a grouping bonded to a vinyl radical. $e < 0$ for electron-donating, and $e > 0$ for electron-accepting substituents. Syrene (substituent = phenyl), for which $e = -1$, is used as a standard.

Stable complexes are formed only with olefins which have $e \geqslant 1.20$. Olefins with $e < 1.20$ [butyl acrylate (1.06), methacrylonitrile (0.81), acrylic acid (0.77), methyl vinyl ketone (0.68), and ethyl acrylate (0.22)] do not give stable olefinic complexes even when L = bipy; in all cases (bipy)Pd(DBA) compounds are formed. It also follows from Table 4 that stable complexes are formed with such good σ-donating and weak π-accepting ligands as bipy and phen; less powerful σ-donors, e.g. tmeda and $P(OR)_3$, form complexes only with a very strong π-acceptor, such as maleic anhydride. The weak σ-donor PPh_3 does not form stable mixed complexes with any of the olefins listed in Table 4; in all cases $Pd(PPh_3)_n$ is formed.

The reactions of olefins with Pt-complexes of DBA are similar[16,66] but as platinum is more nucleophilic than palladium[67] stable olefinic complexes are formed even with phosphines and arsines. The following complexes have been obtained:[39] $(PPh_3)_2Pt$(olefin) (where olefin = 4-phenylbut-3-en-2-one or 1,3-diphenylprop-2-en-1-one), $(PEt_3)_2Pt(CF_2=CF_2)$, and $(AsPh_3)_2Pt(CCl_2=CCl_2)$. Similar complexes are formed in the reaction of $L_2Pt(DBA)$ with olefins.[39] DBA is thus displaced from its complexes by an olefin such as tetrachloroethylene which is capable of displacing stilbene and diphenylacetylene from $(PPh_3)_2Pt$(olefin) complexes.[68,69] In the

sequence indicating the ease of substitution of ligands[60] DBA is placed next to acetylenes:

$$C_2H_4 < C_2H_2 \approx DBA < (CN)_2C{=}C(CN)_2 < (CO \approx PPh_3) < < O_2NC_6H_4C{\equiv}CC_6H_4NO_2.$$

p-Quinones react with $Pd_2(DBA)_3$ in the presence of neutral ligands similarly to olefins, forming L_2Pd(quinone) type complexes,[28] which can also be obtained by reactions of PdL_4 with the corresponding quinones.[70] However, the preparation of π-quinone complexes of palladium via the DBA complexes is more advantageous and gives products with a higher degree of purity and greater yields.

The reaction of olefins with DBA complexes of palladium in the presence of neutral ligands thus gives previously known[67] Pd^0 derivatives; their stability is governed by the delicate electronic balance between the donor and acceptor properties of the neutral ligands and the olefins. Quite recently, by combining electron-donating and electron-accepting olefins, a group of Japanese authors[71,72] has prepared mixed olefinic complexes of Pd^0 by the reaction of $Pd_2(DBA)_3$ with an electron-accepting olefin in the presence of an excess of an electron-donating olefin or diene. The acceptor olefins used were maleic anhydride, dimethyl fumarate, and tetracyanoethylene, and the donor olefins were cyclo-octadiene, norbornadiene, norbornene, and cyclopentene.

New tri-coordinated complexes of Pd^0 have been obtained by this method. Up to the present only two purely olefinic π-complexes of Pd^0 are known: $(cod)_2Pd$, where cod = cyclo-octa-1,5-diene,[73–76] and $(CH_2{=}CH_2)_3Pd$;[73–75] the method for preparing mixed olefinic derivatives proposed in Refs.71 and 72 offers further prospects for obtaining these practically important compounds. The stabilisation of Pd^0 by a combination of electron-donating and electron-accepting olefins evidently plays an important role in the palladium-catalysed cyclotrimerisation reactions between dimethyl acetylenedicarboxylate (an electron acceptor) and norbornadiene or norbornene (electron donors).[77]

(b) Reactions with acetylenes. Another very interesting aspect of the reactivity of DBA complexes of palladium and platinum is their reaction with acetylenes. The investigation of these reactions has provided many fundamentally important results which are of general significance for the chemistry of organometallic compounds of transition metals.

The ability of DBA complexes of palladium and platinum to react with alkynes has been mentioned in earlier work devoted mainly to the study of reactions with olefins.[16,20,39,64]

The reaction of $(PEt_3)_2Pt$(DBA) with hexafluorobutyne in toluene at room temperature over a period of 48 h gives a quantitative yield of the known complex $(PEt_3)_2Pt(CF_3C{\equiv}CCF_3)$.[16] The same product is formed by the reaction of $(DBA)_2Pt$ with an excess of hexafluorobutyne in the presence of triethylphosphine[18,20] or of tetrakis(triethylphosphine)platinum with $CF_3C{\equiv}CCF_3$.[75]

The reaction of acetylenes with DBA derivatives of palladium has been studied more thoroughly. The reaction of $Pd_2(DBA)_3$ with dimethyl acetylenedicarboxylate (dmad) in the absence of phosphorus-containing or any other stabilising ligands leads to the formation of a polymeric cyclopentadiene-palladium complex which was isolated and characterised by its ^1H n.m.r. spectrum.[64]

A similar metalladiene complex of platinum, platinacyclopenta-2,4-diene, is formed by the reaction of dmad with $Pt(DBA)_2$ or $Pt(DBA)_3$.[76] It was not isolated pure but was characterised by the ^1H n.m.r. spectrum and by conversion to the bis(triphenylphosphine) adduct $\{(PPh_3)_2Pt[C(COOMe)]_4\}_n$. These metallacyclopentadiene complexes are suggested to be intermediates in the cyclotrimerisation of acetylenes catalysed by Pd^0 and Pt^0 compounds.[76]

The results of the reaction of $Pd_2(DBA)_3$ with dmad in the presence of *n*-donor ligands depend to a considerable extent on the nature of the ligand used.[64,77] In the case of PPh_3 a bis(triphenylphosphine) complex of Pd^0 with dmad is formed initially; this complex reacts with a second dmad molecule to form palladiacyclopentadiene. $P(OPh)_3$ also reacts with $Pd_2(DBA)_3$ and dmad to give bis(triphenylphosphite)(dmad)palladium(0) in the initial stage but the latter complex is not converted to palladiacyclopentadiene on reaction with excess of the alkyne. However, treatment of the polymeric palladiacyclopentadiene with triphenyl phosphite gives bis(triphenylphosphite)palladiacyclopentadiene as expected. Bidentate *n*-donor ligands (bipy, phen, tmeda, dmg, bte, badn)† react with $Pd_2(DBA)_3$ in the presence of dmad, by-passing the π-acetylene complex stage, and forming the corresponding palladiacyclopentadiene straightaway. It is interesting in this regard that the reaction between bipy, $Pd_2(DBA)_3$, and maleic anhydride takes place with intermediate formation of a π-olefinic complex which is later converted to palladiacyclopentadiene. The stability of the intermediate π-acetylene complex therefore depends on the nature of the *n*-donor ligand, as follows: bipy ≈ phen ≪ PPh_3 < $P(OPh)_3$. In this sequence from left to right there is a marked increase in the π-accepting ability of the ligands which will stabilise the π-acetylenic derivatives of Pd^0.[78]

The palladium complex of TBAA referred to previously reacts with dmad in the presence of bipy to form the bipyridyl complex of palladiacyclopentadiene.[39]

(c) Preparation of enyl type complexes. The ability of DBA derivatives of Pd to form π-allyl complexes by oxidative addition of allyl substrates, which was mentioned in the early work of Japanese authors,[1] is a characteristic property of Pd^0 compounds. μ-Bridging bis-π-allylpalladium halides or cationic π-allyl complexes can be obtained depending on the way the reaction is carried out. For example, the reaction of $Pd_2(DBA)_3$ with methylallyl chloride in benzene gives di-μ-chloro-bis(π-methylallylpalladium);[1] allyl bromide, allyl chloride, but-2-enyl chloride, and cinnamyl chloride react similarly. The rate of oxidative addition varies in the order:[64]

$$C_3H_5Br > C_3H_5Cl > 2\text{-}C_4H_7Cl > 1\text{-}C_4H_7Cl > 3\text{-}PhC_3H_4Cl.$$

For example, the reaction with allyl chloride takes 5 min but with cinnamyl chloride 30 min are required.

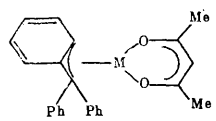
If the complex (bipy)Pd(DBA) is used in the reaction with the allyl halides or $Pd(DBA)_2$ is used in the presence of bipy, then cationic π-allyl complexes of palladium are formed.[64] The reactions of the allyl halides with the complex $(TBAA)_3Pd_3.CHCl_3$ are similar.[39] However, all these reactions are of no practical interest for the preparation of π-allyl complexes of palladium. Unfortunately π-allyl halide compounds of platinum, which are difficult to obtain, cannot be produced by this method. The reaction of DBA complexes of Pt with allyl halides takes place in the presence of donor ligands and gives cationic π-allyl compounds of platinum which are of little interest from a practical point of view.

Allyloxyphosphonium and allylisothiouronium salts react with $Pd_2(DBA)_3$ in a similar way to the allyl halides; in the presence of donor ligands cationic π-allyl complexes of palladium are formed in high yields.[79]

‡dmg = dimethylglyoxime, bte = 1,2-bis(methylthio)ethane, and badn = biacetyldianil.

In all the work quoted above in this section[1,39,64,79] the π-allyl complexes are formed from compounds which already contain an allylic system (allyl halides, allyloxyamidophosphonates, allylisothiouronium salts, etc.), so that the production of π-allylic compounds is not unexpected. On the contrary, in view of the clear tendency of palladium to form π-allylic type complexes,[80] the isolation of π-allylic derivatives from these reactions is a normal result.

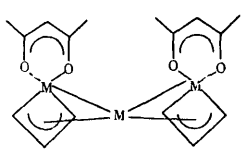
From this point of view the series of papers on the reaction of DBA complexes of palladium and platinum with triphenylmethyl chloride[81-83] and triarylcyclopropenylium bromide[84-86] form a clear contrast. Although the benzyl group is known to be capable of η^3-type bonding with a transition metal atom,[87-92] the formation of a π-allylic ligand from triphenylmethyl precursors has not been established with a sufficient degree of certainty.[93] Complexes of the $\{M[CPh_2(C_6H_4X)]Cl\}_n$ (M = Pd, Pt; X = H, F, OMe) type have been obtained by the reaction of dibenzylideneacetone derivatives of palladium or platinum with substituted triphenylchloromethanes.[82] For these compounds a dimeric structure with a Pd_2Cl_2 bridging fragment was proposed on the basis of the far infrared spectra [ν(M−Cl) = 288 cm^{-1}] and molecular weight determination. X-Ray structure determinations on acetylacetonate derivatives[83] showed that the Pd and Pt compounds are isostructural and there is η^3-coordination of the CPh_3-ligand with the metal atom, i.e. the structure of the complex in the crystalline state is:



M = Pd, Pt

The importance of this work[81-83] is that the results obtained enable the structure of similar nickel complexes, which were prepared as long ago as 1966,[93] to be described correctly.

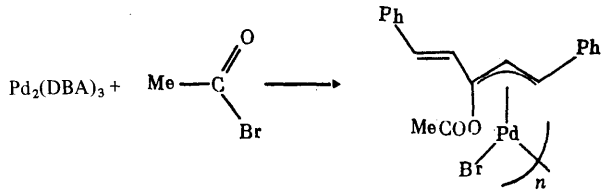
Interesting structure types of η^3-complexes have been reported.[84-86] The reaction of DBA complexes of palladium and platinum with phenyl-substituted cyclopropenylium bromides gives sparingly soluble complexes of the $[M_3(C_3R^1R^2_2)_2Br]$ type which undergo reactions that are typical of complexes with bridging M_2Cl_2 fragments.[86] An X-ray structure determination was carried out on $Pd_3[C_3Ph(p\text{-}MeOC_6H_4)_2]_2(acac)_2$. The structure[85] can be described as two palladiacyclobutenyl "units" $\{(acac)Pd(C_3R^1R^2_2)\}$, with η^3-type bonding of each of them to a third palladium atom:



M = Pd

Thus during the reaction a C−C bond in the cyclopropenyl ring has been broken; in the unsymmetrically substituted phenyldi-(4-methoxyphenyl)cyclopropenylium bromide it is predominantly the $MeOC_6H_4C-CC_6H_4OMe$ bond that is broken.

Another unusual η^3-complex has been obtained by the reaction of $Pd_2(DBA)_3$ with acetyl bromide:[94]



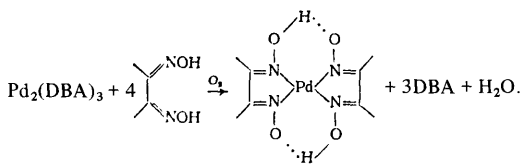
Treatment of this complex with aqueous NaOH regenerates the original $Pd_2(DBA)_3$, reactions with thallium β-diketonates or cyclo-octa-1,5-diene in the presence of $AgPF_6$ lead to cleavage of the μ-bromide bridges and formation of monomeric [(PhCH=CHC(OCOMe)C_2H_2Ph)Pd(acac)] or {[PhCH=CHC(OCOMe).C_2H_2Ph]Pd(cod)]PF_6.

The formation of a π-allylic ligand can be represented as attack by $MeCO^+$ on the oxygen atom of the carbonyl group in DBA; a similar process—the formation of allylic complexes of iron by the reaction of $MeCO^+BF_4^-$ with $Fe[RCH=CHC(O)R^1](CO)_4$—has been reported.[95]

2. Other Reactions of DBA Complexes of Palladium and Platinum

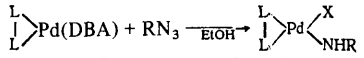
Some of the reactions discussed in this section have been mentioned previously. For example, the total replacement of DBA by phosphines,[16,28] and partial substitution by bipyridyl and phenanthroline[18,21] and also by phosphines and arsines.[16] Below we shall consider reactions of DBA derivatives, mainly those of palladium, which also take place with total or partial replacement of the DBA and lead to the formation of various palladium complexes which are, in a number of instances, difficult or impossible to prepare by other methods. A common feature of the reactions discussed below is oxidation of the metal atom (particularly palladium to form Pd^{II} derivatives), i.e. these processes are essentially reactions in which there is oxidative addition to a complex of palladium in a low-valent state. However, the special properties of DBA complexes lead, in this instance, to unexpected results. For example, the oxidation of triphenylphosphine complexes of zerovalent nickel, palladium, and platinum by oxygen is known to give peroxo-deriva-tives of these metals.[96] The dibenzylideneacetone derivative of palladium does not form peroxo-complexes under these conditions; the oxidation of $Pd_2(DBA)_3$ by oxygen in the presence of bipy gives (bipyridyl)dihydroxopalladium[18,64] and formaldehyde. The forma-tion of formaldehyde in this reaction presupposes the intermediate formation of (bipyridyl)peroxopalladium which is reduced by methanol to the dihydroxo-complex. It is interesting that oxidation of (bipy)Pd(DBA) by the action of 7% H_2O_2 in methanol also gives (bipyridyl)dihydroxopalladium.[64]

The oxidation of $Pd_2(DBA)_3$ by oxygen in the presence of dimethylglyoxime takes place quite differently:[18,64]



All the oxygen is quantitatively used in converting the oxime hydrogen to water; similar reactions are observed with acetylacetone and 8-quinolinol.[64]

In the reaction of (L−L)Pd(DBA), where L−L = bipy or phen, with aroyl- or tosyl azides the DBA ligand is displaced and amide derivatives of palladium(II) are formed:[97]



R=4-MeC_6H_4CO, X=N_3, L—L=bipy;
R=Ts, X=NHTs, L—L=bipy;
R=Ts, X=NHTs, L—L=phen.

(L—L)Pd$(N_3)_2$ type complexes, which were identified by i.r. spectroscopy, are formed as by-products. If the reaction is carried out in methanol instead of ethanol the amount of by-product increases.

Table 5. Use of dibenzylideneacetone complexes of palladium as catalysts.

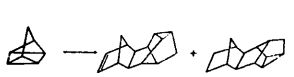
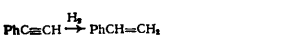
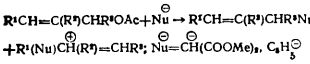
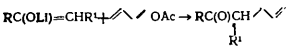
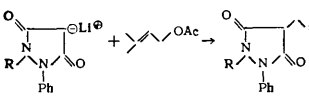
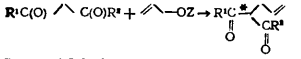
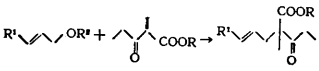
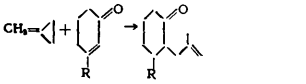
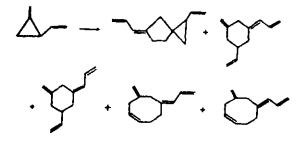
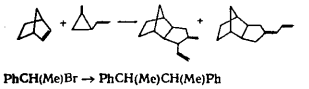
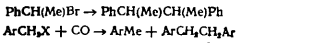
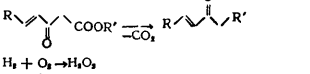
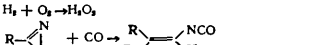
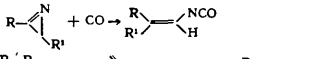
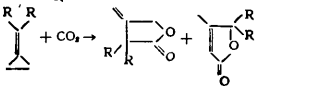
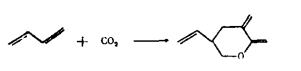
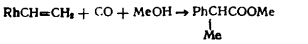
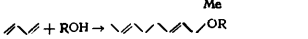
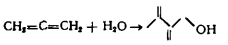
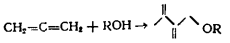
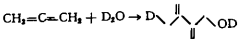
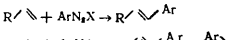
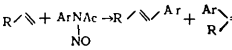
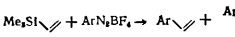
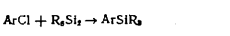
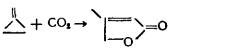
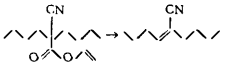
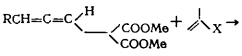
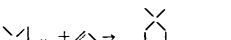
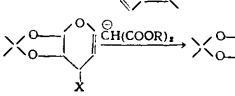
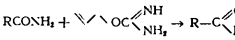
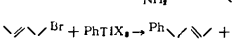
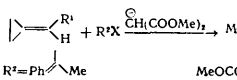
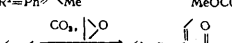
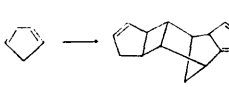
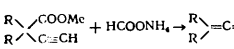
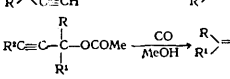
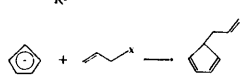
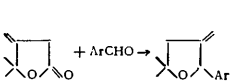
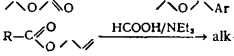
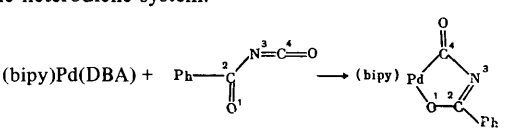
Reaction	Catalyst	Refs.
	$Pd_2(DBA)_3.CHCl_3$	[118]
	$Pd_2(DBA)_3.PhC{\equiv}CH$	[119, 120]
	Pd(DBA)$_2$.DPPE	[121]
	$Pd_2(DBA)_3$.DPPE	[122]
	$Pd_2(DBA)_3$	[123]
	Pd(DBA)$_2$.DIOP	[124]
Z=Me, $PhCH_2$, Ac, Ph		
	$Pd_2(DBA)_3.CHCl_3$.L L = PPh_3, DPPE	[125]
	$Pd_2(DBA)_3.CHCl_3$	[126]
	Pd(DBA)$_2$.PR_3	[127]
	Pd(DBA)$_2$.PR_3	[127]
	$R_4N[Pd(OH)DBA_2]$	[128]
	Pd(DBA)$_2$	[129]
	$Pd_2(DBA)_3.PR_3$	[130]
	Pd(DBA)$_3$	[131]
	Pd(DBA)$_2$	[132]
	Pd(DBA)$_2$.PR_3	[133]
	$Pd_2(DBA)_3$	[134]
	$Pd_2(DBA)_3$	[135]
	$Pd_2(DBA)_3$	[136]

Table 5 (contd.).

Reaction	Catalyst	Refs.
	Pd(DBA)$_2$.PR_3	[137]
	Pd(DBA)$_2$.PR_3	[137]
	Pd(DBA)$_2$.PR_3	[137]
	Pd(DBA)$_2$	[138—140]
	Pd(DBA)$_2$	[141]
	Pd(DBA)$_2$.MeCN	[142]
	$Pd_2(DBA)_3$	[143, 144]
	Pd(DBA)$_2$.PPh_3	[145]
	$Pd_2(DBA)_3.CHCl_3.PPh_3$	[146]
	Pd(DBA)$_2$.DPPE	[147]
	$Pd_2(DBA)_3.CHCl_3.PR_3$	[148]
	Pd(DBA)$_2$.DPPE	[149]
	Pd(DBA)$_2$.DPPE	[150]
	$Pb_2(DBA)_3$	[151]
	$Pd_2(DBA)_3$.diphos	[152]
	$Pd_2(DBA)_3$	[153]
	$Pd_2(DBA)_3$	[154]
	$Pd_2(DBA)_3.PR_3$	[155]
	$Pd_2(DBA)_3.PPh_3$	[156]
	$Pd_2(DBA)_3$	[157]
	$Pd_2(DBA)_3$	[158]
	$Pd_2(DBA)_3.PBu_3$	[159]

Benzoyl isocyanate reacts with (bipy)Pd(DBA) by a completely different route, forming a metallaoxazoline ring by 1,4-addition of Pd^0 to the heterodiene system:[98]

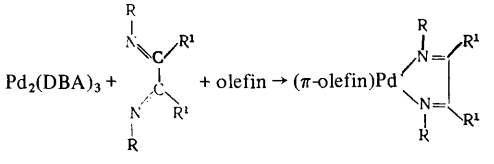


A similar palladiathiazoline complex is formed by the reaction of (bipy)Pd(DBA) with thiobenzoyl isocyanate.[98] The same compound is obtained in a quantitative yield by the reaction of (bipy)Pd(DBA) with 2-phenylthiazoline-4,5-dione.[98] During the reaction CO is liberated vigorously; it is assumed[98] that a palladiathiazine derivative is formed initially and this is converted to the palladiathiazoline complex with elimination of carbon monoxide. However, under the same conditions the biacetylanil derivative of dibenzylideneacetonepalladium reacts with phenylthiazoline-4,5-dione without elimination of CO, giving a 76% yield of the palladiathiazoline complex. This complex does not eliminate CO even on heating.

The use of dibenzylideneacetone complexes to obtain various σ-derivatives of palladium and platinum is described in a series of papers.[100–106]§ σ-phenyl complexes of palladium with sterically hindered phenoxy groups have been synthesised by the Reutov–Sokolov method (see Ref.108); the preparation of σ-palladiated complexes by using $Pd(DBA)_3$ has been reported.[109–115]

In all the reactions listed above in this section there is oxidative addition of the various substrates to Pd^0 with formation of Pd^{II} derivatives. There are two reports in which DBA compounds of Pd^0 react either without a change in the formal oxidation state of the palladium[114] or with the formation of formally univalent palladium derivatives.[115]

In Ref.114 complexes of palladium with 1,4-diazabutadienes were obtained starting from $Pd_2(DBA)_3$, $Pd_3(TBAA)_3$, and $Pd_3(TTAA)_3$ (TTAA = tritoluylideneacetylacetone) which was synthesised by the authors. However, the anticipated (1,4-diazabutadiene)Pd(DBA) type complexes could not be isolated because they are too unstable. In the opinion of these authors[114] the reason for the instability of such compounds is the imbalance between the electron-donating and electron-accepting properties of 1,4-diazabutadiene and DBA. Whereas the former is a strong σ-donor, the π-accepting properties of DBA are clearly insufficient to reduce the electron density on the metal atom. To stabilise the complexes it is necessary to use either less basic diazabutadienes or ligands which are better π-acceptors than dibenzylideneacetone. Hence the principles governing the choice of ligand will be approximately the same as in the preparation of π-olefinic complexes of Pd^0 starting from $Pd_2(DBA)_3$ (see above). In fact, the introduction of strongly electron-accepting substituents into the 1,4-diphenyldiazabutadiene molecule led to the formation of a stable Pd^0 compound. On the other hand, the use of electron-accepting olefins [tetracyanoethylene (TCNE), maleic anhydride (MA), dimethyl fumarate (DMF), and diethyl fumarate (DEF)] as co-reagents enables olefin-diazabutadiene complexes of Pd^0 with more basic diazabutadienes to be obtained:



R = Bu^t, R^1 = H, olefin = TCNE; R = Bu^t, R^1 = H, olefin = MA; R = Pr^i, R^1 = H, olefin = MA; R = cyclo-C_6H_{11}, R^1 = H, olefin = MA; R = cyclo-C_3H_5, R^1 = Me, olefin = DMF; R = 4-$MeOC_6H_4$, R^1 = H, olefin = DMF; R = 4-$MeOC_6H_4$, R^1 = H, olefin = DEF; R = Bu^t, R^1 = H, olefin = DMF; R = Bu^t, R^1 = H, olefin = DEF; R = Pr^i_2CH, R^1 = H, olefin = DMF.

§For more detail see the review in Ref.107.

A comparison of these results with those in Table 4 shows that all the diazabutadienes used have σ-donor properties which surpass those of such strong σ-donors as trimethyl and triphenyl phosphite and resemble those of tetramethylethylenediamine.

The reaction of $Pd_2(DBA)_3$ with an excess of MeNC gives solutions which are stable in the absence of air and which react with iodine to give the Pd^{II} derivative $(MeNC)_2PdI_2$. The $Pd_2(DBA)_3$/MeNC system is concluded to be a synthetic equivalent of $Pd(MeNC)_x$ species. The reaction of $Pd_2(DBA)_3$ and methyl isocyanide with $[(MeNC)_4Pd](PF_6)_2$ gives dimeric Pd^I complexes in a good yield.[115]

Similar dimers containing Pd–Pd, Pd–Pt, and Pd–Mn bonds have been obtained.[116,117]

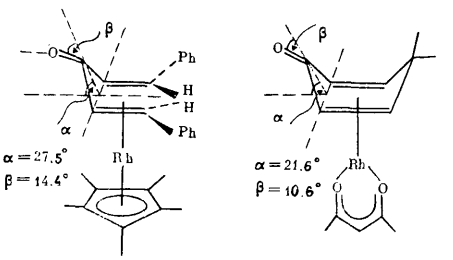
VI. USE OF DBA COMPLEXES OF THE PLATINUM METALS AS HOMOGENEOUS CATALYSTS

DBA complexes, particularly those of palladium, have recently been intensively studied as catalysts of very varied reactions. An attempt to classify this work is made in Table 5.

It appears from the examples given in this table that catalysis by DBA complexes of palladium in essence differs little from catalysis by other Pd^0 complexes[160,161] but the use of DBA catalysts is to be preferred because of their easy accessibility and the simplicity of working with them.

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The bulk of the work on the chemistry of DBA complexes of transition metals and determination of their structures was carried out in the period 1971–1974 and subsequent publications relate mainly to their use as reagents, catalysts, etc. DBA derivatives of palladium and platinum are now firmly established in preparative organometallic chemistry as highly reactive starting materials suitable for the synthesis of the most diverse classes of organo-Pd and organo-Pt compounds. However, the DBA molecule may be of interest in organometallic chemistry not only as an olefinic or dienone ligand as such but also as a model structural fragment in a number of more complex organic molecules of other classes. For example, metal complexes with semi-quinonoid π-ligands can be regarded[162] as unusual "closed" analogues of DBA complexes like $(DBA)RhC_5Me_5$,[26] as follows:



The validity of this analogy is confirmed by the considerable similarity observed in the angles α and β, which characterise the conformational changes in the dienone system resulting from π-coordination of the double bonds to the transition metal atom.[162]

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